

SHOSTAKOVSKIY, M.F.

Ionie polymerization of vinyl ethers. M. F. Shostakovskii, I. I. Mikhaut'ev, and N. N. Gochinnikova (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izv. Akad. Nauk S.S.S.R., Khim. Nauk* 1953, 1054-60; cf. *CA*: 48, 12668c. —  $ROCH_2CH_3$  were polymerized by treatment with a trace of 5%  $FeCl_3 \cdot 6H_2O$  in BuOH (vigorous reaction). The polymers, which were sol. in the usual org. solvents, had the following properties (% yield,  $d_4^{25}$ ,  $n_D^{25}$ , and mol. wt., resp., given): (R shown): *Et*, 68, 0.9123, 1.4641, 2545; *Pr*, 79, 0.9570, 1.4520, 5634; *Bu*, 92, 1.4523, 4830; *iso-Bu*, 61, 0.9263, 1.4520, 4560; *Bu*, 92, 0.9250, 1.4570, 4738; *iso-Bu*, 90, 0.9205, 1.4505, 4183; *iso-AM*, 86, 0.9117, 1.4607, 4048; *C<sub>6</sub>H<sub>5</sub>*, 89, 0.9120, 1.4632, 4003; *cyclohexyl*, 92, 0.9364, 1.4891, 1545; *C<sub>12</sub>H<sub>25</sub>*, 0.9132, 1.4651, 3909; *C<sub>18</sub>H<sub>37</sub>*, 89, 0.9230, 1.4607, 4262; *isodetyl*, 93, 0.9207, 1.4661, 3261; *C<sub>18</sub>H<sub>37</sub>*, 87, 0.9118, 1.4670, 3799; *C<sub>18</sub>H<sub>37</sub>*, 80, 0.9282, 1.4682, 5138.

G. M. Kosolapoff

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SHOSTAKOVSKIY, M.F.

Derivatives of unsaturated tertiary alcohols. I. Synthesis of acetylenic acetals based on vinyl ethers and acetylenic alcohols. M. F. Shostakovskii and I. A. Shikhiev (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1953, 1081-7. —To 42 g.  $\text{Me}_2\text{C}(\text{OH})\text{C}\equiv\text{CH}$  and 72 g.  $\text{EtOCH}:\text{CH}_2$  (which failed to react alone) was added 0.02 ml. 30%  $\text{HCl}$  and the mixt. allowed to stand overnight; distn. after drying with  $\text{K}_2\text{CO}_3$  gave 79.5%  $\text{MeCH}(\text{OEt})\text{OCMe}_2\text{C}\equiv\text{CH}$ ,  $b_{12-13}$  42-3°,  $d_{20}$  0.8701,  $n_D^{20}$  1.4162, readily hydrolyzing in 2%  $\text{H}_2\text{SO}_4$  to  $\text{AcH}$ ,  $\text{EtOCH}:\text{CH}_2$ , and a moderate yield of  $\text{MeCH}(\text{OCMe}_2\text{C}\equiv\text{CH})_2$  (I),  $b_1$  70-82°,  $d_{20}$  0.8976,  $n_D^{20}$  1.4468. Similarly  $\text{iso-PrOCH}:\text{CH}_2$  gave 70.5%  $\text{MeCH}(\text{OCHMe}_2)\text{OCMe}_2\text{C}\equiv\text{CH}$ ,  $b_{12}$  153-5°,  $b_{12-13}$  47-8°,  $d_{20}$  0.8568,  $n_D^{20}$  1.4150. Heating this acetal (42.5 g.) with 42 g.  $\text{Me}_2\text{C}(\text{OH})\text{C}\equiv\text{CH}$  in a sealed tube 52 hrs. at 170-80° gave a little  $\text{iso-PrOH}$ , 20.7 g.  $\text{Me}_2\text{C}(\text{OH})\text{C}\equiv\text{CH}$  and 49.4 g. crude (32% pure) I,  $b_{12}$  74-6°,  $d_{20}$  0.8967,  $n_D^{20}$  1.4412.  $\text{iso-BuOCH}:\text{CH}_2$  similarly gave 78.2%  $\text{MeCH}(\text{OCH}_2\text{CHMe}_2)\text{OCMe}_2\text{C}\equiv\text{CH}$ ,  $b_{12}$  173-4°,  $b_{12-13}$  55-6°,  $d_{20}$  0.8587,  $n_D^{20}$  1.4170.  $\text{BuOCH}:\text{CH}_2$  similarly gave 81.5%  $\text{MeCH}(\text{OBu})\text{OCMe}_2\text{C}\equiv\text{CH}$ ,  $b_{12}$  181-2°,  $b_{12-13}$  62-3°,  $n_D^{20}$  1.4182,  $d_{20}$  0.8592. The Bu and  $\text{iso-Bu}$  derivs. were most stable thermally in respect to disproportionation. G. M. Kosolapoff.

1. SHOSTAKOVSKIY, M. F., SIDE'KOVSKAYA, F. P.

2. U33R (600)

4. Lactams

7. Activation of vinylcaprolactam in the presence of hydrogen peroxide. Izv.  
AN SSSR. Otd. khim. nauk. no. 1, 1953

9. Monthly List of Russian Accessions, Library of Congress, June 1953. Unclassified.

SHOSTAKOVITSIY, K. Ye.; GARGHEVYI, K. A.; VOLKOVA, Z. S.

Glycols

Transformations of vinyl ethers. Part 8. Transformations of ethylene glycol acetals  
Izv. AN SSSR. Otd. khim. nauk No. 1, 1953.

Monthly List of Russian Accessions, Library of Congress, June 1953. Uncl.

SHOSTAKOVSKI, M. F.

6  
②  
Comparison of the action of metallic chlorides on polymerisation.  
1. Catalysis of polymerisation of styrene by ferric and stannic  
chlorides. M. F. Shostakovskii and V. A. Gladyshevskaya (*Izvestia*,  
1953, No. 2, 351-358). In the presence of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , styrene  
does not polymerise in  $\text{N}_2$ , and forms polystyrene and benzaldehyde  
in air, whereas in presence of  $\text{SnCl}_4$  it polymerises in both  $\text{N}_2$  and air.  
R. C. MURRAY.

SHOSTAKOVSKIY, M.F.; PRILEZHAYEVA, Ye.N.; SHAPIRO, Ye.S.

Synthesis of sulfur compounds based on vinyl ethers and acetylene. Part  
6. Reaction of mercaptans with vinyl ethers. Izv. AN SSSR. Otd.khim.  
nauk. no.2:357-367 Mr-Apr '53. (MLA 6:5)

1. Institut organicheskoy khimii Akademii nauk SSSR.  
(Mercaptans) (Vinyl ethers)

SHOSTAKOVSKIY, M.F.; CHEKULAYEVA, I.A.

Synthesis and transformations of vinyl ethers of ethanolamines. Part 3.  
Nature of the double bond of vinyl ethers of ethanolamines. Izv. AN SSSR.  
Otd.khim.nauk. no.2:368-373 Mr-Apr '53. (MLRA 6:5)

1. Institut organicheskoy khimii Akademii nauk SSSR. (Vinyl ethanolamine)

SHOSTAKOVSKIY, M. F.  
 Synthesis of mixed ethers and polyethers of polyvalent  
 alcohols. A. P. Meshcheryakov, M. P. Shostakovskii,  
 and P. V. Tyunayev (Inst. Org. Chem., Acad. Sci. U.S.S.R.,  
 Moscow). *Sbornik Statei Oshcheli Khim.* 2, 824-30  
 (1953).—Hydrogenation of alkyl vinyl ethers over Bag Al-  
 Ni alloy catalyst (cf. *C.A.* 31, 1000<sup>9</sup>) readily yields the cor-  
 responding mixed ethers. The catalyst is prepd. by treat-  
 ment of 150 g. 50% Al-Ni alloy with 500 ml. 4% NaOH, then  
 with a similar amt. of NaOH after subsidence of the reaction,  
 and 2 more similar aunts. after 3-4 hrs. The catalyst retains  
 appreciable amts. of Al, thus differing from the conventional  
 Raney Ni. The hydrogenations were run at 80-140 atm. H  
 and gave about 95% yields of the satd. ethers. Thus,  
 BuOCH:CH<sub>2</sub> gave EtOBu; (CH<sub>3</sub>OCH:CH<sub>2</sub>)<sub>2</sub> gave (CH<sub>3</sub>-  
 OEt)<sub>2</sub>, and (CH<sub>3</sub>CH<sub>2</sub>OCH:CH<sub>2</sub>)<sub>2</sub> gave (CH<sub>3</sub>CH<sub>2</sub>OEt)<sub>2</sub>, b  
 165-6.5°, d<sub>4</sub> 0.8420, n<sub>D</sub><sup>20</sup> 1.4050. G. M. Kosolapoff

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AB Jan



SHOSTAKOVSKIY, M. F.

~~CZECH~~

✓ Synthesis and transformations of vinyl aryl ethers. III.  
 Synthesis of aralkyl and diaryl acetals. M. F. Shostakov-  
 skii, A. V. Kalabina, and A. D. Dariev (State Univ., Ir-  
 kutsk). *Sbornik Statei Obshchei Khim.* 2, 1297-1301 (1955),  
 cf. C.A. 42, 72434; 43, 3272a. — Treatment of mixts. of *p*-  
 Me<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>OH and alkyl vinyl ether with a little HCl yielded  
 mixts. which on distn. gave 51-76% yields of the correspond-  
 ing mixed acetals and low yields of the sym. diaryl acetal;  
 the same products were obtained on heating the phenol with  
*p*-Me<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>3</sub> in an autoclave 12 hrs. at 220-5°.  
 The following MeCH(OR)OC<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>-*p*(R, b.p.<sup>o</sup>/mm.,  
 n<sub>D</sub><sup>20</sup>, d<sub>4</sub> given) were reported: Me, 72-3°/4, 1.4620, 0.9600;  
 Et, 127-8°/4, 1.4875, 0.9520; Pr, 85-6°/2, 1.4830, 0.9383;  
 Bu, 155-6°/10, 1.4850, 0.9343; Bu, 125-6°/4, 1.4705,  
 0.9317; Am, 122-3°/2, 1.4910, 0.9257; PA, 145-7°/3,  
 1.5370, 1.0283; MeCH(OC<sub>6</sub>H<sub>4</sub>Me<sub>2</sub>-*p*), 161-2°/3, n<sub>D</sub><sup>20</sup> 1.5110,  
 d<sub>4</sub> 0.9448. G. M. Kosolapoff

SHOSTAKOVSKIY, M.F.; MIKHANT'YEV, B.I.; OVCHINNIKOVA, N.N.

Indirect vinylation of monocarbonic acids and oxyacids. Izv. AN SSSR Otd.  
khim.nauk no.3:556-561 My-Je '53. (MLRA 6:8)

1. Institut organicheskoy khimii Akademii nauk SSSR. (Esters)

SHOSTAKOVSKIY, M.F.; GERSHTEYN, N.A.

Conversions of vinyl ethers. Chemical properties of alkyl- $\beta$ -chloroethyl-acetals. Izv. AN SSSR. Otd.khim.nauk no.4:716-720 JI-Ag '53. (MLRA 6:8)

1. Institut organicheskoy khimii akademii nauk SSSR. (Vinyl compounds)

SHOSTAKOVSKIY, M.F.; MIKHANT'YEV, B.I.; OVCHINNIKOVA, N.N.

Ionic copolymerization of vinyl ethers. Izv. AN SSSR, Otd. khim. nauk no. 4:  
721-725 11-ag '53. (MLBA 6:8)

1. Institut organicheskoy khimii Akademii nauk SSSR.  
(Polymers and polymerization) (Vinyl ethers)

SHOSTAKOVSKIY, M. S.

USSR/ Chemistry - Synthesis

Card 1/1 ; Pub. 40 - 20/22

Authors : Shostakovskiy, M. S.; Shikhiev, I. A.; and Kochkin, D. A.

Title : Synthesis and conversions of oxygen-containing silicon-organic compounds. Part 1.- Synthesis of silicon-organic acetals

Periodical : Izv. AN SSSR. Otd. khim. nauk 5, 941-944, Sep-Oct 1953

Abstract : A new synthesis of O-containing silicon-organic compounds, based on the reaction of vinyl ethers and silanols, is discussed. It was established for the first time that triethylsilanol condenses with vinylbutyl and vinylisobutyl ethers in conditions analogous to corresponding syntheses with organic alcohols. The synthesis of hitherto unknown nonsymmetrical butyl- and isobutyltriethylsilaneacetals, is described. A new method for the derivation of various silicon-organic acetals, is presented. Three USSR references (1933-1952).

Institution : Academy of Sciences, Institute of Organic Chemistry

Submitted : December 23, 1952

SHOSTAKOVSKIY, M.F.; SHIKHIYEV, I.A.; KOCHKIN, D.A.

Investigation in the field of synthesis and conversions of silicon organic compounds containing oxygen. Report no.1: Synthesis of silicon-organic acetals. Izv.AN SSSR Otd.khim.nauk no.5:941-944 S-O '53. (MLRA 6:10)

1. Institut organicheskoy khimii Akademii nauk SSSR.  
(Acetals) (Silicon organic compounds)

SHOSTAKOVSKIY, M.F.; KHOMUTOV, A.M.

Research in the field of chemical conversions of unsaturated and high molecular weight compounds. Report no.1. Copolymerization of methacrylic acid and vinylalkyl ethers. Izv.AN SSSR, Otd.khim.nauk no.6: 1048-1055 N-D '53. (MLRA 6:12)

1. Institut organicheskoy khimii Akademii nauk SSSR.  
(High molecular weight compounds) (Methacrylic acid) (Ethers)

SHOSTAKOVSKIY, M.F.; MIKHANT'YEV, B.I.; OVCHINNIKOVA, N.N.

Ionic polymerization of vinyl ethers. Izv.AN SSSR. Otd.khim.nauk no.6:  
1056-1060 N-D '53. (MLBA 6:12)

1. Institut organicheskoy khimii Akademii nauk SSSR.  
(Vinyl ethers) (Polymers and polymerization)



SHOSTAKOVSKIY, M.F.; SHIKHIYEV, I.A.

Research in the field of the derivatives of tertiary unsaturated alcohols. Report no.1. Synthesis of acetylene acetals based on vinyl ethers and acetylene alcohols. Izv.AN SSSR. Otd.khim.nauk no.6:1061-1067 N-D '53. (MLRA 6:12)

1. Institut organicheskoy khimii Akademii nauk SSSR.  
(Acetals) (Acetylene derivatives) (Ethers)

SHOSTAKOVSKY, M. F.

Analytical Abst.  
Vol. 1 No. 2  
Feb. 1954  
Organic Analysis

(2) Chem  
306. Methods of analysis of halogenated ethers.  
I. Analysis of  $\alpha$ -halogen-dialkyl and ethylaryl  
ethers. M. F. Shostakovsky and A. V. Bordanova  
(*J. Anal. Chem., U.S.S.R.*, 1953, 8 [4], 231-234).  
Compounds of the type  $RCH_2CHXOR'$  where  
 $R = H$  or  $CH_3$ ,  $X = Cl$  or  $Br$ , and  $R' =$  Alkyl or  
Aryl are hydrolysed instantaneously at room temp.  
to  $RCH_2CHO$ ,  $HX$  and  $R'OH$  by excess of water.  
Detection of the compounds can be based on tests  
for aldehyde, halide, or acid. They can be deter-  
mined by hydrolysis followed by titration with  
0.1 N NaOH, titration with 0.1 N  $AgNO_3$ , or  
titration of the aldehyde with bisulphite. A  
number of different compounds were determined  
in this way with excellent results. G. S. SMITH.

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9-22-54

SHOSTAKOVSKIY, M. F.

Chem Abs

1.48 25 Jan 54

Organic Chem

Decomposition of benzoyl peroxide in the medium of some vinyl compounds. M. F. Shostakovskii, E. P. Gracheva, and V. A. Neterman. *Zhur. Obshchei Khim.* 23, 54-60(1953).— $Bz_2O_2$  (12 g.) in 72.1 g.  $CH_2=CHOAc$  and 120 g. petr. ether heated to  $80-7.5^\circ$  in N atm. over 5 hrs. gave 0.7480 g. O, 0.0384 g.  $CO_2$ , and 0.0366 g.  $H_2O$ , with 94.33% decompn. leading to O formation. The secondary source of  $CO_2$  appears to be destructive oxidation of  $CH_2=CHOAc$ . Similar reaction in the presence of  $CH_2=CMeCO_2Me$  gave 0.4043 g. O, 0.0171 g.  $CO_2$ , and 0.0542 g.  $H_2O$ , while the reaction in the presence of  $PhCH=CH_2$  gave 0.0738 g.  $CO_2$ . The reaction in the presence of  $CH_2=CHOAc$  gave some  $BzOH$ , polyvinyl acetate,  $AcOH$ , and  $AcH$ . With  $CH_2=CMeCO_2Me$  the by-products included polymethyl methacrylate, while the reaction in the presence of  $PhCH=CH_2$  run similarly at  $86^\circ$  gave only 3.38% decompn. of the peroxide to  $CO_2$ . Heating 100 g.  $BuOCH=CH_2$  and 12 g.  $Bz_2O_2$  33 hrs. gave 97.7 g. unchanged  $BuOCH=CH_2$ , and 4.7 g. product,  $b_p$   $74-5^\circ$ ,  $n_D^{20}$  1.4040,  $d_4^{20}$  0.8260, and 13.1 g. viscous solid, besides 3.75 g.  $BzOH$ . The distd. product analyzed as  $C_{10}H_{12}O_4$ . Thus peroxides like  $Bz_2O_2$  serve as supply of both free radicals and O, the latter being able to serve as a chain initiator in polymerization reactions of vinyl deriv. present in the system. Vinyl ethers are not polymerized by these means as they are not polymerized by atm. O. G. M. Kosolapoff

SHOSTAKOVSKIY, M.F.

/ Acetylenic alcohols and glycols. I. Synthesis and transformations of 1,4-butyne-1,3-diol. M. F. Shostakovskii and A. V. Bogdanova. *J. Gen. Chem. U.S.S.R.* 23: 67-61 (1953) (Engl. translation).—See *C.A.* 48, 12416.

H. L. H.

SHOSTAKOVSKIY, M.F.; GRACHEVA, Ye.P.

Investigation in the field of synthesis and conversions of substituted vinyl ethers. Part 1. Synthesis of  $\alpha$ -substituted vinyl ethers. Zhur.ob. khim. 23 no.7:1153-1158 J1 '53. (MLRA 6:7)

1. Institut organicheskoy khimii Akademii Nauk SSSR. Laboratoriya vini-  
lovykh efirov. (Ethers) (Vinyl derivatives)

SHOSTAKOVSKIY, M.F.; MIKHANT'YEV, B.I.; OVCHINNIKOVA, N.N.; NETERMAN, V.A.

Synthesis of incomplete acylals of lactic acid. Zhur.ob.khim. 23 no.7:  
1167-1173 J1 '53. (MLRA 6:7)

1. Institut organicheskoy khimii Akademii Nauk SSSR.  
(Lactic acid) (Ethers)

STOS TAYOCHNY, "P.

Synthesis and transformations of  $\alpha$ -methylvinyl butyl ether. II. M. P. Shostakovskii and R. P. Gracheva. *Zhur. Obshchei Khim.* 23, 1320-3 (1953); cf. *C.A.* 47, 12217c. —Heating 111 g. BuOH, 50 g. MeC<sub>2</sub>CH, and 10 g. powd. KOH in an autoclave 14 hrs. at 248-50° (58 atm. max. pressure) gave 75.8% CH<sub>3</sub>CMeOBu, bp 111-12°, n<sub>D</sub><sup>20</sup> 1.4111, d<sub>4</sub><sup>20</sup> 0.7955. When shaken 1 hr. with 1% H<sub>2</sub>SO<sub>4</sub>, it is completely hydrolyzed, yielding Me<sub>2</sub>CO. The ether (11.4 g.) and 7.4 g. BuOH stirred 30-40 min. and treated with 2 drops concd. HCl reacted exothermically and distn. of the mixture gave 81% Me<sub>2</sub>C(OBu)<sub>2</sub>, bp 70°, n<sub>D</sub><sup>20</sup> 1.4150, d<sub>4</sub><sup>20</sup> 0.8363. This is completely hydrolyzed by shaking 1 hr. with 1% H<sub>2</sub>SO<sub>4</sub>, yielding Me<sub>2</sub>CO. G. M. Kosolapoff

SHOSTAKOVSKIY, M. F.

U S S R .

✓ Azeotropic mixtures of vinyl alkyl ethers with alcohols.  
II. M. F. Shostakovskii, E. N. Polezhaeva, and N. I.  
Uvarova. *J. Appl. Chem. U.S.S.R.* 26, 1003-8 (1953)  
(Engl. translation). See *C.A.* 48, 10534d. H. L. H.



SHOSTAKOVSKIY, M.F.; PRILEZHAYEVA, Ye.N.; UVAROVA, N.I.

Azeotropic mixtures of vinylalkyl ethers and alcohols. Zhur.prikl.khim. 26  
no.10:1074-1079 0 '53. (MLRA 6:10)

1. Institut organicheskoy khimii Akademii nauk SSSR. Laboratoriya vinilovykh  
soyedeneniy. (Azeotropy) (Vinyl ethers) (Alcohols)

SHOSTAKOVSKIY, M. F.

Chemical Abst.  
Vol. 48  
Apr. 10, 1954  
Organic Chemistry

Optical study of the hydrogen bond in some monovinyl ethers of glycols and polyglycols. M. F. Shostakovskiy, M. I. Batuev, P. V. Tyupacy, and A. D. Matveeva. *Doklady Akad. Nauk S.S.S.R.* 89, 601-4 (1953). The Raman spectra of monovinyl ethers of glycol,  $\text{CH}_2(\text{CH}_2\text{OH})_n$ ,  $\text{O}(\text{CH}_2\text{CH}_2\text{OH})_n$ , and  $(\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH})_n$  show a long-wave displacement of the OH frequency with typical smearing of the band at  $3200-800\text{ cm}^{-1}$ . Cryoscopic mol. wts. also show assocn. increasing with increased concn. of the ethers in  $\text{C}_6\text{H}_6$ ; the isomeric cyclic acetals of glycol,  $\text{CH}_2(\text{CH}_2\text{OH})_2$ , and  $(\text{CH}_2\text{CH}_2\text{OH})_2$ , which cannot form H bonds also show lower b.ps. and lower viscosities than are shown by their isomers; vinyl glycol ethers. The latter show isomerization into the acetals in solns. in  $\text{CCl}_4$ ; this does not occur in  $\text{C}_6\text{H}_6$ . G. M. Kosolapoff

SHOSTAKOVSKIY, M. F. - BATUEV, M. I. - TIUPAEV, P. V. - MATVEYEVA, A. D.

Oxonium

Oxonium theory and its optical substantiation on simple vinyl ethers.  
Dokl. AN SSSR 89 no. 1, 1953

9. Monthly List of Russian Accessions, Library of Congress, May 1953. Unclassified.

SHOSTAKOVSKIY, M. F.

Synthesis and transformations of oxygen-containing silicoorganic compounds. Synthesis of methyl, ethyl, and isopropyl triethylsilane acetals. M. F. Shostakovskii, K. A. Andrianov, I. A. Shikhiev, and D. A. Kochkin. *Doklady Akad. Nauk S.S.S.R.* 93, 691-3 (1953); cf. preceding abstr. —Heating 33 g.  $\text{Et}_3\text{SiOH}$ , 19 g.  $\text{MeOCH}_2\text{CH}_3$  and 0.02 ml. 30%  $\text{HCl}$  in sealed tube 6.5 hrs. at  $65^\circ$  gave 68.0%  $\text{MeCH(OEt)OSiEt}_3$ ,  $b_p$   $74-5^\circ$ ,  $n_D^{20}$  1.4235,  $d_4^{20}$  0.8720. To 33 g.  $\text{Et}_3\text{SiOH}$  and 30 g.  $\text{EtOCH}_2\text{CH}_3$  was added 0.02 ml. 30%  $\text{HCl}$  and the mixt. was heated 1 hr. to  $50^\circ$  and left overnight; after drying it gave 45.1%  $\text{MeCH(OEt)OSiEt}_3$ ,  $b_p$   $78-9^\circ$ ,  $n_D^{20}$  1.4232,  $d_4^{20}$  0.8032. Similarly iso- $\text{PrOCH}_2\text{CH}_3$  and  $\text{Et}_3\text{SiOH}$  with 30%  $\text{HCl}$  catalyst gave after 8.5 hrs. in a sealed tube at  $65^\circ$  gave 42%  $\text{MeCH(OCHMe)OSiEt}_3$ ,  $b_p$   $87-9^\circ$ ,  $d_4^{20}$  0.8561,  $n_D^{20}$  1.4238. G. M. Kosolapoff

SHOSTAKOVSKIY, M. I.

USSR

Synthesis and transformations of unsaturated organo-silicon compounds. I. Synthesis of vinylsilane chlorides by a direct method. M. F. Shostakovskii and D. A. Kochkin. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1954, 145-6 (Engl. translation).—See C.A. 49, 6090b.

H. L. H.

SHOSTAKOVSKIY, M. F.

U.S.S.R.

Stabilization of  $\alpha$ -halogenated ethers. M. F. Shostakovskii and A. V. Bogdanova (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1954, 182-5. Satisfactory stabilization for several months or years of  $\text{EtOCHMeCl}$ ,  $\text{EtOCHMeBr}$ , and  $\text{BuOCHMeBr}$  is attained by adding to them of 15-20%  $\text{Et}_2\text{O}$ . For stabilization at elevated temp. (2 months at  $60^\circ$ ) the amt. of added  $\text{Et}_2\text{O}$  must be about 50%. Dioxane is less effective, as is  $\text{C}_6\text{H}_6$ , although both show some protective action.  
G. M. Kosolapoff

SHOSTAKOVSKIY, M. F.

USSR.

✓ Reaction of vinyl and polyfunctional compounds. I. Reaction of vinyl alkyl ethers with glycerol. M. F. Shostakovskii, V. V. Zhebrovskii, and M. A. Medelyanovskaya (Inst. Org. Chem. Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1954, 166-72; *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1954, 137-41 (English translation).—Stirring 14.4 g.  $\text{EtOCH}_2\text{CH}_2$  and 18.4 g. glycerol 0.5 hr. and adding 1 drop  $\text{HCl}$  catalyst gave an exothermic reaction (temp. rise to  $76.5^\circ$ ), after which the mixt. was neutralized and distd., yielding 7.5 g. mixed  $\text{EtOH}$  and  $\text{MeCH}(\text{OEt})_2$  and 17.8 g. crude product,  $b_p$   $70-93^\circ$ , which could not be resolved into pure components. This with  $\text{BzCl}$  in pyridine gave 5.8 g. solid benzoate (I) and 11.30 g. liquid benzoate (II); I was identified as 1,3-ethylideneglycerol benzoate,  $m$   $85^\circ$ , and II as the 1,2-ethylidene isomer,  $b_p$   $101-2^\circ$ ,  $d_{20}$  1.1558,  $n_D^{20}$  1.5140. I heated with 10%  $\text{KOH}$  until a clear soln. formed and the cooled soln. satd. with  $\text{K}_2\text{CO}_3$  and extd. with  $\text{Et}_2\text{O}$  yielded 35% 1,3-ethylideneglycerol,  $b_p$   $66-8^\circ$ ,  $n_D^{20}$  1.4520,  $n_D^{25}$  1.4538. II similarly gave 43% 1,2-ethylideneglycerol,  $b_p$   $84-5^\circ$ ,  $n_D^{20}$  1.4436.  $\text{EtOCH}_2\text{CH}_2$  (3 moles) treated with 1 mole glycerol did not form these derivs.; the products were  $\text{EtOH}$ ,  $\text{MeCH}(\text{OEt})_2$ , and bis(ethylideneglycerol). To 25.04 g.  $\text{BuOCH}_2\text{CH}_2$  and 23 g. glycerol was added 3 drops  $\text{HCl}$  catalyst and the mixt. heated 0.5 hr. to  $50^\circ$ , at which point an exothermic reaction took place; after neutralization the mixt. yielded 11.87 g.  $\text{BuOH}$  and 23 g. crude product,  $b_p$   $85-103^\circ$ , which, benzoylated as above, yielded 4.2 g.  $\text{BuOBz}$  and 29.98 g. II; no I was found. It is believed that the reaction proceeds through formation of mixed acetals with subsequent cyclization to the final products. G. M. Kosolapoff.

SHOSTAKOVSKIY, M. F.

USSR.

✓ Synthesis and transformations of unsaturated organosilicon compounds. I. Synthesis of vinylsilane chlorides by a direct method. M. F. Shostakovskii and D. A. Keshkin (Inst. Org. Chem. Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1954, 174-5. — An Fe pipe (50 mm. by 100 cm.) was charged with 1.5 kg. 20:80 Cu-Si alloy in 10-15 mm. pieces, heated to 350-400° 50 min. in a dry N stream for drying, and  $\text{CH}_3\text{CHCl}$  passed in at 0.1 l./min. because of uneven temp. distribution, coke formation developed in parts of the tube; after 80 hrs. there was collected 750 g. product, which on fractionation yielded 20.3%  $\text{CH}_2=\text{CHSiCl}_3$ ,  $b_p$  92.5-4.0°,  $d_4$  1.2050, and about 9%  $(\text{CH}_2=\text{CH})_2\text{SiCl}_2$ ,  $b_p$  118-19°,  $d_4$  1.0813. G. M. Kosolapov



SNOSTAKOVSKIY, M.F.

Synthesis of sulfur compounds from vinyl ethers and acrylonitrile. VII. Peculiarities of the addition reaction of hydrogen sulfide to vinyl butyl ether against the Markovnikov rule. M. F. Snostakovskiy, E. N. Prilezhnev, and G. S. Shumilo (N. D. Zelinski Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izv. Akad. Nauk S.S.S.R., Khim. Nauk* 1954, 202-203; cf. C.A. 48, 9311; Addn. of H<sub>2</sub>S to BuOCH:CH<sub>2</sub> is catalyzed by small amounts of O<sub>2</sub>, which leads to contra-Markovnikov order of addn.; acrylonitrile and some peroxides also give this result. Larger amounts of O<sub>2</sub>, Br<sub>2</sub>O<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub> inhibit the reaction, probably by chain breaking through oxidation of chain-leading radicals RSCl<sub>2</sub>C(OR)H. Heating 1 mole BuOCH:CH<sub>2</sub>S, while an equimolar mixt. in the cold yields BuSCH<sub>2</sub>CH<sub>2</sub>SH. BuOCH:CH<sub>2</sub>S stored for a long time over Na and showing a peroxide test reacts very sluggishly, but BuOCH:CH<sub>2</sub>S stored over K<sub>2</sub>CO<sub>3</sub> reacts normally. A good catalytic effect is produced by addn. of small amounts of HCl in dioxane. VIII. General method of synthesis of  $\beta$ -alkoxymethylmercaptans. *Ibid.* 303-13. Reaction of H<sub>2</sub>S and ROCH:CH<sub>2</sub> in the presence of traces of O yields the corresponding alkoxyethylmercaptans and corresponding sulfides, predominantly on contra-Markovnikov structure, especially noted in derivatives. Branched ethers tend to give the normal addition products. Keeping 15 g. BuOCH:CH<sub>2</sub>S and 0.7 g. H<sub>2</sub>S in sealed tube 10 days gave 88.9% BuSCH<sub>2</sub>CH<sub>2</sub>SH, b. 126-8°, n<sub>D</sub><sup>20</sup> 1.4456, d<sub>4</sub><sup>20</sup> 0.9112, and 5.1 g. EtOCH:CH<sub>2</sub>S, with former yields 85.8% EtSCH<sub>2</sub>CH<sub>2</sub>SH, b. 91-3°, n<sub>D</sub><sup>20</sup> 1.4378, d<sub>4</sub><sup>20</sup> 0.9227, and a mixture of (PrOCH:CH<sub>2</sub>)<sub>2</sub>S each of the latter obtained by distillation; mpn. of the latter with H<sub>2</sub>Cl<sub>2</sub> gave the pure former sulfide, b. 113-4°, n<sub>D</sub><sup>20</sup> 1.4393, d<sub>4</sub><sup>20</sup> 0.9394, whose H<sub>2</sub>Cl<sub>2</sub> adduct m. 69-70°. Reaction of

[illegible]

SHOSTAKOVSKIY, M-F

USSR 1 / Some reactions which proceed during the processes of  
polymerization of vinyl butyl ether: M. P. Shostakovskiy  
and V. A. Gladyshevskaya. *Bull. Acad. Sci. U.S.S.R.,  
Div. Chem. Sci.* 1954, 299-304 (Engl. translation).—See  
*C.A.* 49, 4508a. H. L. H.

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① M. P. Shostakovskiy

SHOSTAKOVSKIY, M. F.

# USSR

✓ Synthesis and transformations of vinyl ethers of ethanolamines. IV. Copolymerization of vinyl ether of 2-aminoethanol and methyl ester of methacrylic acid. M. F. Shostakovskii, I. A. Chekulaeva, and A. M. Khomutov (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1954, 323-8; cf. *C.A.* 48, 6704t. — Pure  $\text{CH}_2=\text{CHO}-\text{CH}_2\text{CH}_2\text{NH}_2$  does not polymerize under action of  $\text{Bz}_2\text{O}_2$  in 100 hrs. at  $80^\circ$ . In mixts. with Me methacrylate it copolymerizes in varying proportions, yielding products contg. 0.25-5.3% N; the copolymers with appreciable amts. of N are generally insol. and infusible. No polymer of Me methacrylate usually forms in the course of copolymerization, but the yields of the copolymer are usually quite low. Expts. with copolymerization yielded varying amts. of  $\text{CH}_2=\text{CHOCH}_2\text{CH}_2\text{NHCH}_2\text{CHMeCO}_2\text{Me}$ ,  $b_p$   $97.5^\circ$ ,  $n_D^{20}$  1.4491,  $d_4^{20}$  0.9998, which hydrogenated over Raney Ni to the said analog,  $b_p$   $82^\circ$ ,  $n_D^{20}$  1.4333,  $d_4^{20}$  0.9668.

G. M. Kosolapoff

SHOSTAKOVSKIY, M.F.

# USSR.

Some reactions which proceed during the processes of polymerization of vinyl butyl ether. M. F. Shostakovskii and V. A. Gladyshevskaya (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1954, 382-9. Heating 100 g. of a mixt. of 92% BuOCH:CH<sub>2</sub> and 8% BuOH with 0.24 g. 5% FeCl<sub>3</sub> in BuOH at 100° 2 hrs. gave MeCH(OBu)<sub>2</sub> and a yellow polymer composed of 18% low mol. wt. material (mol. wt. av. 692) and 74% high mol. wt. material (av. 2112). The av. mol. wt. of the product can be controlled to some extent by addn. of BuOH in the course of polymerization for the purpose of chain-breaking. A reaction of 1 mole BuOCH:CH<sub>2</sub> and 0.5 mole BuOH yielded in addition to MeCH(OBu)<sub>2</sub> and the polymer, a small amt. of MeCH(OBu)CH<sub>2</sub>CH(OBu)<sub>2</sub>, b<sub>p</sub> 137-8°, n<sub>D</sub><sup>20</sup> 1.4259, d<sub>4</sub><sup>20</sup> 0.8661, which was also readily prepd. by the reaction of BuOCH:CH<sub>2</sub> with MeCH(OBu)<sub>2</sub> in BuOH in the presence of FeCl<sub>3</sub> at 48-50°. G. M. Kosolapoff

SHOSTAKOVSKIY, M-F

USSR

Chemical transformations of unsaturated and high-molecular compounds. II. Copolymerization of methyl ester of methacrylic acid with vinyl alkyl ethers. M. F. Shostakovskii and A. M. Kholmutoy. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1954, 411-15 (Engl. translation).—*Sci. C.A.* 48, 14291k. H. L. H.

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SHOSTAKOVSKIY, M.F.

✓ Transformations of vinyl aryl ethers. I. Ionic polymerization of vinyl aryl ethers. A. V. Bogdanova and M. F. Shostakovskii. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1954, 789-95 (Engl. translation). II. Radical polymerization and copolymerization of vinyl aryl ethers. M. F. Shostakovskii and A. V. Bogdanova. *Ibid.* 797-801. — See *Chem. Abstr.* 49:13241i. B. M. R.

SHOSTAKOVSKIY, M. F.

CH Chemical transformations of unsaturated high molec-  
ular weight compounds. III. Copolymeriza- on of meth-  
acrylic acid and its methyl ester with vinyl benzyl ether.  
M. F. Shostakovskii and A. M. Khramov. Bull. Acad.  
Sci. U.S.S.R., Div. Chem. Sci. 1954, 803-7 (Engl. transla-  
tion). See C-1-49, 13031b. B. M. P.

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SHOSTAKOVSKIY, M. F.

Derivatives of unsaturated tertiary alcohols. II. Synthesis of methyl, ethyl, isopropyl, and butyl dimethyl(vinyl)carbinyl acetals. M. F. Shostakovskii and I. A. Shikhiev. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1954, 809-12 (Engl. translation). III. Synthesis of dimethyl(ethynyl and vinyl)carbinyl and methylethyl(ethynyl and vinyl)carbinyl *tert*-butyl acetals. M. F. Shostakovskii, I. A. Shikhiev, and V. I. Belyayev. *Ibid.* 821-4.—See C.A. 49, 13390d. B. M. R.

SHOSTAKOVSKI, M.F.

✓ Transimerizations of vinyl aryl ethers. I. Ionic polymerization of vinyl aryl ethers. A. V. Bogdanova and M. F. Shostakovskii (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izv. Akad. Nauk S.S.S.R., Khim. Nauk*, 1954, 911-18. — PhOCH<sub>2</sub>CH<sub>3</sub> (10 g.) and 0.15 g. catalyst (FeCl<sub>3</sub>, AlCl<sub>3</sub>, or BF<sub>3</sub>·Et<sub>2</sub>O, or 1 ml. 8% FeCl<sub>3</sub> in dioxane, or 0.5 ml. 10% BF<sub>3</sub>·Et<sub>2</sub>O in Et<sub>2</sub>O) were kept in ampuls at 15-18°; increase of viscosity became rapidly apparent (most rapid with BF<sub>3</sub>); similar results were obtained after 1-2.5 hrs. refluxing. The resulting polymers had low mol. wt. (383-354) and were very viscous liquids, except for the one prepd. with AlCl<sub>3</sub> catalyst in which case the polymer m. 40-2°, and had mol. wt. 405. Prepn. of the polymer with BF<sub>3</sub> catalyst at reflux under 2.5 mm. pressure gave the only colorless polymer. Fractionation of the crude products resulted in isolation of: diphenyl acetal and a solid fragile product, m. 45-7°, corresponding to (C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>C<sub>2</sub>H<sub>4</sub>; Mol. dist. gave a viscous (C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>CH<sub>2</sub> and solid (C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>CH<sub>2</sub>, m. 45-50°. p-Me<sub>2</sub>CC<sub>6</sub>H<sub>3</sub>OC<sub>2</sub>H<sub>5</sub>CH<sub>3</sub> with FeCl<sub>3</sub> catalyst gave 92% light-colored solid, m. 42-1°, corresponding to (C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>, similar to that obtained with BF<sub>3</sub> catalyst at room temp. With BF<sub>3</sub> catalyst at reflux under vacuum there was formed 80.7% solid polymer, m. 40-1°, corresponding to (C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>. II. Radical polymerization and copolymerization of vinyl aryl ethers. M. F. Shostakovskii and A. V. Bogdanova. *Ibid.* 919-23. — The use of [CMe<sub>2</sub>(CN)N]: as catalyst has resulted in successful polymerization of ArOCH<sub>2</sub>CH<sub>3</sub>, as well as in their copolymerization. PhOCH<sub>2</sub>CH<sub>3</sub> in 100 hrs. with 4% catalyst at 75° gave 21.6% crude polymer, which yielded on fractionation a solid product, m. 53-73°, corresponding to (C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>C<sub>2</sub>H<sub>4</sub> and one, m. 44-5°, corresponding to (C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>C<sub>2</sub>H<sub>4</sub>. Similarly, p-Me<sub>2</sub>CC<sub>6</sub>H<sub>3</sub>OC<sub>2</sub>H<sub>5</sub>CH<sub>3</sub> gave 17.6% polymer, m. 48-6°, corresponding to (C<sub>6</sub>H<sub>5</sub>O)<sub>2</sub>C<sub>2</sub>H<sub>4</sub>. A mixt. (1:1) of PhOCH<sub>2</sub>CH<sub>3</sub> and BuOCH<sub>2</sub>CH<sub>3</sub> with 2% catalyst gave 9.7% copolymer contg. 90.5% PhOCH<sub>2</sub>CH<sub>3</sub> units. With PhOCH<sub>2</sub>CH<sub>3</sub>-BrOCH<sub>2</sub>CH<sub>3</sub> the product (9.3%) contained 71.05% PhOCH<sub>2</sub>CH<sub>3</sub> units, while BuOCH<sub>2</sub>CH<sub>3</sub>-p-Me<sub>2</sub>CC<sub>6</sub>H<sub>3</sub>OC<sub>2</sub>H<sub>5</sub>CH<sub>3</sub> gave an 11% yield of product contg. 73% ArOCH<sub>2</sub>CH<sub>3</sub> units. The products had low mol. wt. (530-740). The usual radical mechanism with Me<sub>2</sub>C(CN)<sub>2</sub> initiator is proposed. G. M. P. (Lapal)

SHOSTAKOVSKI, M.F.

62 ✓ Chemical transformations of unsaturated and high molecular weight compounds. III. Copolymerization of methacrylic acid and its methyl ester with vinyl phenyl ether. M. F. Shostakovskii and A. M. Khomutov (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1954, 924-30; cf. *C.A.* 49, 8961a.—Copolymerization of  $\text{PhOCH}:\text{CH}_2$  with  $\text{CH}_2:\text{CMeCO}_2\text{H}$  (I) and its Me ester (II) were run at  $60^\circ$  in the presence of 0.2%  $\text{Bz}_2\text{O}_2$ ; a 1:1 ratio of the ether and II gave a copolymer sol. In 1:1  $\text{BuOH-PhOCH}:\text{CH}_2$ . At 1/3 ratio of II and  $\text{PhOCH}:\text{CH}_2$ , the copolymer was formed similarly and its sol. was similar to the above. As the proportion of  $\text{PhOCH}:\text{CH}_2$  in the initial mixt. was raised from 25% to 75%, the content of  $\text{PhOCHCH}_2$  unit in the copolymer rose from 11.5 to 34.6%, but the yield of the copolymer declined from 76% to 10.66%. The abs. viscosity of the product declined from 0.021 to 0.0031, and relative viscosity from 2.89 to 1.00. Interaction of I and  $\text{PhOCH}:\text{CH}_2$  in 3/1 ratio gave a 10% yield of product, contg. 57.88% I units. At 1:1 proportion of reactants, the product contained 42% I units and had mol. wt. 2265, while at 1:3 reactant proportion the product contained 53.5% I units. The liquid residue contained appreciable smts. of  $\text{CH}_2:\text{CMeCO}_2\text{CHMeOPh}$ . The results indicate that along with copolymerization side reactions take place which result in formation of acylals. G. M. Kosolapoff

SHOSTAKOVSKIY, M-F.

Derivatives of unsaturated tertiary alcohols. II. Synthesis of methyl, ethyl, isopropyl, and butyl dimethylvinyl acetals. M. F. Shostakovskii and I. A. Shikhiev (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Invest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1954, 931-5; cf. *C.A.* 49, 2307f. — To 21.5 g.  $\text{Me}_2\text{C}(\text{OH})\text{CH}:\text{CH}_2$  and 18 g.  $\text{MeOCH}:\text{CH}_2$  was added at  $-12^\circ$  0.016 ml. 30%  $\text{HCl}$  and the mixt. heated in sealed tube 9.5 hrs. at  $85^\circ$  to give after neutralization with  $\text{K}_2\text{CO}_3$  78%  $\text{MeOCHMeO}:\text{CMe}_2\text{CH}:\text{CH}_2$ ,  $b_{\text{p}}$  28-9°,  $b_{\text{m}}$  132-3°,  $n_D^{20}$  1.4130,  $d_4^{20}$  0.8601. Letting 43 g.  $\text{Me}_2\text{C}(\text{OH})\text{CH}:\text{CH}_2$  and 36 g.  $\text{EtOCH}:\text{CH}_2$  stand overnight with 0.013 ml. 30%  $\text{HCl}$  similarly gave 82.82%  $\text{EtOCHMeOCMe}_2\text{CH}:\text{CH}_2$ ,  $b_{\text{p}}$  40-1°,  $b_{\text{m}}$  146-7°,  $n_D^{20}$  1.4118,  $d_4^{20}$  0.8502. Similarly were prepd.: 79%  $\text{iso-PrOCHMeOCMe}_2\text{CH}:\text{CH}_2$ ,  $b_{\text{p}}$  46-6°,  $b_{\text{m}}$  156-7°,  $n_D^{20}$  1.4126,  $d_4^{20}$  0.8422, and 80.8%  $\text{BuOCHMeOCMe}_2\text{CH}:\text{CH}_2$ ,  $b_{\text{p}}$  182-3°,  $b_{\text{m}}$  0.8396,  $n_D^{20}$  1.4148. III. Synthesis of dimethylethynyl(vinyl) and methylethylethynyl(vinyl) *tert*-butyl acetals. M. F. Shostakovskii, I. A. Shikhiev, and V. I. Belyaev. *Ibid.* 945-8; cf. *C.A.* 49, 8111s. — Addn. of 0.02 ml. 30%  $\text{HCl}$  to 24.5 g.  $\text{MeEtC}(\text{OH})\text{C}(\text{CH}_3)_2\text{CH}:\text{CH}_2$  and 25 g.  $\text{Me}_2\text{COCH}:\text{CH}_2$ , followed by 5 min. at  $70-5^\circ$  and 12 hrs. at room temp. gave 69.6%  $\text{Me}_2\text{COCHMeOCMe}_2\text{EtC}(\text{CH}_3)_2\text{CH}:\text{CH}_2$ ,  $b_{\text{p}}$  88-9°,  $d_4^{20}$  0.8694,  $n_D^{20}$  1.4290. Similarly were prepd.: 72.5%  $\text{Me}_2\text{COCHMeOCMe}_2\text{C}(\text{CH}_3)_2\text{CH}:\text{CH}_2$ ,  $b_{\text{p}}$  68-9°,  $d_4^{20}$  0.8692,  $n_D^{20}$  1.4264; 81%  $\text{Me}_2\text{COCHMeOCMe}_2\text{CH}:\text{CH}_2$ ,  $b_{\text{p}}$  65°,  $d_4^{20}$  0.8532,  $n_D^{20}$  1.4256; 74%  $\text{Me}_2\text{COCHMeOCMe}_2\text{EtC}(\text{CH}_3)_2\text{CH}:\text{CH}_2$ ,  $b_{\text{p}}$  79-81°,  $d_4^{20}$  0.8540,  $n_D^{20}$  1.4260. The ethynyl derivs. are relatively less stable than their vinyl analogs; the former yellow in storage. G. M. Kosolapoff

SHOSTAKOVSKIY, M.F.; PRILEZHAYEVA, Ye.N.; SHAPIRO, E.S.

Synthesis of sulfurous substances based on vinyl esters and acetylene. Report no.8. General method for the synthesis of  $\beta$ -alkoxyethyl-mercaptans. Izv. AN SSSR. Otd.khim.nauk no.2:303-313 Mr-Ap '54.  
(MLRA 7:6)

1. Institut organicheskoy khimii im. N.D.Zelinskogo Akademii nauk SSSR.  
(Mercaptans)

USSR/Chemistry      Copolymerization

Card : 1/1

Authors : Shostakovskiy, M. F., and Khomutov, A. M.

Title : ~~Study of chemical conversions of unsaturated and high-molecular compounds.~~  
Part 2.- Copolymerization of methyl methacrylate and vinyl alkyl ethers

Periodical : Izv. AN SSSR, Otd. Khim. Nauk., 3, 484 - 490, May - June 1954

Abstract : The copolymerization of methyl acrylate and vinyl alkyl ethers was investigated at different ratios under the effect of benzoyl peroxide. The copolymeric products obtained are described. Benzoyl peroxide promotes the copolymerization of vinyl alkyl ethers with compounds containing multiple  $C = C - C = O$  bonds. The reason for not finding methyl methacrylate polymers during the polymerization under the effect of benzoyl peroxide is explained. Sixteen references: 11 USSR; 1 German, 4 USA. Tables.

Institution : Acad. of Sc. USSR, The N. D. Zelinskiy Institute of Organic Chemistry

Submitted : March 20, 1953

*SHOSTAKOVSKIY, M.F.*

USSR/Chemistry

Quantitative analysis

Card : 1/1

Authors : Shostakovskiy, M. F., and Prilezhaova, E. N.

Title : Synthesis of sulfurous compounds on acetylene and vinyl ether bases.  
Part 9.- Synthesis and certain properties of beta-alkoxyethylvinyl sulfides

Periodical : Izv. AN SSSR, Otd. Khim. Nauk. 3, 517 - 525, May - June 1954

Abstract : A method for the synthesis of beta-alkoxyethylvinyl sulfides from beta-alkoxy methyl mercaptanes is described. A newly introduced method for quantitative determination of thiovinyl ethers, based on their decomposition reaction in the presence of mercuric chloride, is analyzed. A study of the chemical properties of beta-alkoxyethylvinyl sulfides showed that the reactions of thiovinyl ethers are much different than the reaction of their oxygen analogues. Sixteen references: 11 USSR, 4 USA and 1 German. Tables.

Institution : Acad. of Sc. USSR, The N. D. Zelinskiy Institute of Org. Chemistry

Submitted : Feb 10, 1953

*SHOSTAKOVSKIY, M. F.*

USSR/ Chemistry      Sulfurous compounds

Card : 1/1

Authors : Shostakovskiy, M. F., Prilezhaeva, E. N., and Uvarova, N. I.

Title : Synthesis of sulfurous compounds on the vinyl ether and acetylene basis.  
Part 10.- Synthesis and certain conversions of vinylethyl sulfide.

Periodical : Izv. AN SSSR, Otd. Khim. Nauk. 3, 526 - 534, May - June 1954

Abstract : Conditions favorable for the synthesis of vinylethyl sulfide with a yield of 60%, were established. The addition of mercaptan and hydrogen sulfide to vinylethyl sulfide when exposed to air, and the polymerization of the latter in the presence of  $\text{FeCl}_3$  and  $\text{SnCl}_2$  ion catalysts, are analyzed. The formation of mercurated ethylmercaptan salt was determined during the reaction of vinylethyl sulfide with mercuric chloride in alcohol and water solutions. The formation of an unstable complex salt, decomposing in water or alcohol, was established during the reaction in an ether solution. Twenty-two references: 10 USSR, 8 German, 4 USA. Tables.

Institution : Acad. of Sc. USSR, The N. D. Zelinskiy Institute of Org. Chemistry

Submitted : February 10, 1953



SHOSTAKOVSKIY, M. F.

Reactions between vinyl and polyfunctional compounds. II.  
Reaction of simple vinyl ethers with polyvinyl alcohol. M. F.  
Shostakovskii, V. V. Zhebrovskii, and M. A. Medvedevskaya  
(Izvest. Akad. Nauk SSSR, *Oklet. khim. Nauk*, 1954, No. 3, 535--  
540).—Vinyl butyl and vinyl phenyl ethers react with polyvinyl  
alcohol to produce polyacetals of polyvinyl alcohol. The reaction  
mechanism is discussed. R. C. MURRAY.

SHOSTAKOVSKIY, M. F.

## USSR/Chemistry      Synthesis

Card            : 1/1      Pub. 40 - 15/27

Authors        : Shostakovskiy, M. F., and Bogdanova, A. V.

Title          : Investigation of acetylene alcohols and glycols. Part 3.- Multistage synthesis of acetals of acetylene glycols

Periodical     : Izv. AN SSSR. Otd. khim. nauk 4, 677 - 682, July - August 1954

Abstract       : Experimental data are presented showing the multistage mechanism of the formation of diacetals of acetylene glycols. The two basic methods - catalytic and thermal - by which multistage synthesis of diacetals is realized, are described. Symmetrization, which intensifies with the increase of molecular weights of the radicals of the basic vinyl ethers, was observed during the derivation of mixed diacetals from homologous monoacetals. It was established that symmetrical diacetal is a product of substitution of the low-molecular alkoxy group by a high-molecular group. Seventeen references: 12 USSR; 3 French; 1 USA and 1 German (1912 - 1954). Tables.

Institution    : Acad. of Sc. USSR, The N. D. Zelinskiy Institute of Organic Chemistry

Submitted      : September 21, 1953

SHOSTAKOVSKIY, M. F.

USSR/ Chemistry      Reaction processes

Card                : 1/1      Pub. 40 - 16/27

Authors            : Shostakovskiy, M. F., Zhebrovskiy, V. V., and Medelyanovskaya, M. A.

Title               : Investigation of reactions of vinyl and polyfunctional compounds. Part  
3.- Reaction of trivinylglycerin ether with ethylene glycol and 1,4-  
butylene glycol

Periodical        : Izv. AN SSSR. Otd. khim. nauk 4, 683 - 688, July - August 1954

Abstract          : The reaction process, in the case when both components (trivinylglycerin  
ether - ethylene- and 1,4-butylen glycols) are polyfunctional compounds  
was investigated. The ratio of the basic reaction components was found  
to be of great importance in the yield of reaction products. A vinyl  
ether surplus, which has the same effect as the reverse order of adding  
reagents, leads to displacement of the reaction toward cyclization of  
the monoacetal. The formation of cyclic acetals of glycols and glycerin  
is explained by the tautomerism of the acetals. Eight references:  
6 USSR; 1 USA and 1 German (1890 - 1954).

Institution       : Acad. of Sc. USSR, The N. D. Zelinskiy Institute of Organic Chemistry

Submitted        : May 20, 1953

SHOSTAKOVSKIY, M. F.

USSR/ Chemistry      Hydrolysis

Card                : 1/1      Pub. 40 - 17/27

Authors            : Shostakovskiy, M. F., Sidel'kovskaya, F. P., and Zelenskaya, M. G.

Title              : Ion hydrolysis of vinyl lactams in an acid medium

Periodical        : Izv. AN SSSR. Otd. khim. nauk 4, 689 - 693, July - August 1954

Abstract         : Ion hydrolysis of vinyl caprolactam and vinylpyrrolidone, was investigated under the effect of sulfuric acid. Lactams and acetaldehyde were found to be the products of ion hydrolysis. A method of quantitative determination of vinyl caprolactam and vinyl pyrrolidone, is described. The effect of acid concentration and temperature on the percentage yield of the hydrolysis products, is explained. Seven references: 6 USSR and 1 German (1900 - 1953). Tables.

Institution : Acad. of Sc. USSR, The N. D. Zelinskiy Institute of Organic Chemistry

Submitted        : May 8, 1953

SHOSTAKOVSKIY, M. F.

USSR/Organic Chemistry - Synthetic Organic Chemistry, E-2

Abst Journal: Referat Zhur - Khimiya, No 19, 1956, 61593

Author: Shostakovskiy, M. F., Shikhiyev, I. A.

Institution: None

Title: Investigations of the Syntheses and Conversions of Organosilicon Compounds. Communication I. Synthesis of the Vinyl Ether of  $\gamma$ -hydroxypropyltrimethylsilane

Original  
Periodical: Izv. AN SSSR, otd. khim. n., 1954, No 4, 745-747

Abstract: Using  $\gamma$ -hydroxypropyl trimethylsilane (I) as an example the possibility has been ascertained of vinylating organosilicon alcohols. I was prepared by passing for 2.5 hours gaseous ethylene oxide (2 mol) into a cooled to  $-6^{\circ}$  Grignard reagent (from 1 g-atom Mg in 800 ml absolute ether and 1 mol  $\alpha$ -chloromethyl trimethylsilane), yield 77.3%, BP  $62-63^{\circ}/10$  mm  $n_D^{20}$  1.4298,  $d_4^{20}$  0.8408. The vinyl ether of  $\gamma$ -hydroxypropyl trimethylsilane  $CH_2 = CH-OCH_2CH_2CH_2Si(CH_3)_3$  (II) obtained on heating in autoclave (8 hours,  $180^{\circ}$ ) a reaction

Card 1/2

USSR/Organic Chemistry - Synthetic Organic Chemistry, E-2

Abst Journal: Referat Zhur - Khimiya, No 19, 1956, 61593

Abstract: mixture consisting of 20 g I, 2 g KOH and 60 g absolute dioxane, saturated with  $C_2H_2$  (18-20 atm,  $20^\circ$ ), yield of II 35%, BP  $60^\circ/18$  mm,  $n_D^{20}$  1.4286,  $d_4^{20}$  0.8168

Card 2/2

SHOSTAKOVSKIY, M. F.

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3041\* Investigation in the Field of the Conversion of  
Vinylaryl Esters. *Issledovanie v oblasti prevrashchenii vinyl-  
arilovykh estrov. II. Radical Polymerization and Copoly-  
merization of Vinylaryl Esters. Radiatsionnaya polimerizatsiya  
i kopolimerizatsiya vinilarylovykh estrov.* (Russian.) M. F.  
Shostakovskii and A. V. Bogdanova. *Izvestia Akademii Nauk  
SSSR, Otdel'noe Khimicheskikh Nauk*, 1954, no. 5, Sept.-Oct.,  
p. 919-923.  
Includes tables, 7 ref.

*SHOSTAKOVSKIY, M.F.*

SHOSTAKOVSKIY, M.F.; SHIKHIYEV, I.A.; BELYAYEV, V.I.

Investigation in the field of derivatives of tertiary unsaturated alcohols. Report no.3. Synthesis of dimethylacetylenyl(vinyl)- and methylethylacetylenyl(vinyl)-tert-butyl acetals. Izv. AN SSSR Otd.khim. nauk no.5:945-948 S-O '54. (MLRA 8:3)

1. Institut organicheskoy khimii Akademii nauk SSSR.  
(Acetals)



*Shostakovskiy, M.F.*  
USSR/Chemistry - Analytical chemistry

Card <sub>1/2</sub> Pub. 40 - 22/27

Authors : Shostakovskiy, M. F.; Batuyev, M. I.; Tyupayev, P. V.; and Matveyeva, A. D

Title : The oxonium theory and the optical study of the hydrogen bond in some monovinyl ethers of glycols and polyglycols

Periodical : Izv. AN SSSR. Otd. khim. nauk 6, 1103-1110, Nov-Dec 1954

Abstract : An optical study was conducted on several monovinyl ethers of liquid glycols and poly glycols to determine whether the valence of the oxygen in these compounds is variable and whether the intermolecular hydrogen bond is stable. The existence of the intermolecular hydrogen bond was also confirmed by other physico-chemical investigations.

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Institute of Organ. Chemistry

Submitted : September 10, 1953

Periodical : Izv. AN SSSR. Otd. khim. nauk 6, 1103-1110, Nov-Dec 1954

Card 2/2 Pub. 40 - 22/27

Abstract : The presence of the intermolecular hydrogen bond explained by the "abnormality" of the valence of the oxygen atom in the investigated ethers (its oxonium nature), and the chemical properties of these ethers. Eight USSR references (1940-1953). Table; graphs.

*SHOSTAKOVSKIY, M. F.*

USSR/ Chemistry - Synthesis

Card  $\frac{1}{2}$  Pub. 40 - 23/27

Authors : Shostakovskiy, M. F., and Chekulayeva, I. A.

Title : ~~Synthesis and conversions of vinyl ethers of ethanol amines.~~ Part 5

Periodical : Izv. AN SSSR. Otd. khim. nauk 6, 1111-1118, Nov-Dec 1954

Abstract : The processes occurring during the vinylation of di- and triethanol amines were investigated. It was found that the vinylation of above mentioned amines leads to the synthesis of complete and incomplete vinyl ethers. Experiments showed that vinyl ethers of diethanol amine and beta-aminoethanol do not submit to cyclization during the synthesis.

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Institute of Org. Chemistry

Submitted : December 23, 1953

Periodical : Izv. AN SSSR. Otd. khim. nauk 6, 1111-1118, Nov-Dec 1954

Card 2/2 Pub. 40 - 23/27

Abstract : Certain chemical conversions of vinyl ethers of di- and triethanol amines were studied and their structure were analyzed. The vinyl ethers in ion conversions were seen to be less reactive than non-substituted vinylalkyl ethers. The tendency of the ethers toward polymerization is explained. Ten references: 7 USSR, 2 USA and 1 German (1931-1954). Tables.

*Shostakovskiy, M. F.*

USSR/Chemistry - Synthesis

Card 1/1      Pub. 40 - 25/27

Authors : Shostakovskiy, M. F.; Kochkin, D. A.; and Vlasov, V. M.

Title : Synthesis and conversions of oxygen-containing silicon-organic compounds

Periodical : Izv. AN SSSR. Otd. khim. nauk 6, 1120-1123, Nov-Dec 1954

Abstract : An investigation was conducted to determine the reaction between ethylene oxide and trialkyl(aryl)silane chlorides : trimethyl-, dimethylethyl-, tri-ethyl- and diethylphenylsilane chlorides. The derivation of 2-chloroethoxy dimethyl-, methyldiethyl- triethyl- and diethylphenylsilanes and their chemical characteristics are described. A new method for the derivation of oxygen-containing silicon-organic compounds is described. Five references: 3 USSR and 2 USA ( 1941-1954 ). Table.

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Institute of Organ. Chemistry

Submitted : July 12, 1954

SHOSTAKOVSKY, M.F.

2446. Methods of analysis of halogenated ethers.  
II. Analysis of  $\alpha\beta$ -dihalogeno- and  $\alpha\beta\gamma$ -trihalo-  
geno-alkyl ethers. M. F. Shostakovsky and E. P.  
Sidelkovskaya (*J. Appl. Chem., U.S.S.R.*, 1954,  
9 [2], 105-108).—Dichloro- and trichloroethyl  
alkyl ethers are hydrolysed by water alone giving  
HCl, which can be titrated with alkali or with  
AgNO<sub>3</sub>. G. S. SMITH

SHOSTAKOVSKIY, M.F., professor; KONONOV, N.F.

Acetic acid manufacture. Khim.v shkole 9 no.6:15-23 N-D '54.  
(Acetic acid) (MLRA 8:1)

SHOSTAKOVSKIY, M-F.

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U S S R .

✓ Methods of analysis of simple halogenized ethers. II.  
Analysis of  $\alpha, \beta$ -dihalo and  $\alpha, \beta$ -trihaloalkyl ethers. M. F.  
Shostakovskii and R. P. Sidel'kovskaya. *J. Anal. Chem.*  
*U.S.S.R.* 9, 117-20 (1954) (Engl. translation).—See *C.A.* 48,  
6916a. H. L. H.



SHOSTAKOVSKIY, M.F.; SHIKHIYEV, I.A.; VLASOV, V.M.; BELYAYEV, V.I.

Synthesis of vinylisopropyl, vinyldibutyl and vinyldiamyl ethers  
and their conversions. Dokl. AN Azerb. SSR 10 no.7:473-482 '54.  
(MLRA 8:10)

1. Predstavleno deystvitel'nyy chlenom Akademii nauk Azerbaydzhan-  
skoy SSR Yu.G.Mamedaliyevym.  
(Vinyl polymers)

SHOSTAKOVSKIY, M.F.; SHIKHIYEV, I.A.; BELYAYEV, V.I.

Investigation in the field of synthesis of derived tertiary unsaturated alcohols. Dokl. AN Azerb. SSR 10 no. 11: 759-765 '54.  
(MLRA 8:10)

1. Predstavleno deystvitel'nym chlenom Akademii nauk Azerbaydzhanskoy SSR Yu. G. Mamedaliyevym.  
(Alcohols)

SHOSTAKOVSKIY, M. F.

USSR/Chemistry - Physical chemistry

Card 1/1 Pub. 43 - 50/62

Authors : Kasatochkin, V. I.; Shostakovskiy, M. F.; Zil'berbrand, O. I.; and Kochkin, D. A.

Title : About hydrogen bonds in silanols

Periodical : Izv. AN SSSR. Ser. fiz. 18/6, 726-728, Nov-Dec 1954

Abstract : The infrared absorption spectra of trimethylcarbinol and five different silanols:  $(CH_3)_3SiOH$ ,  $(CH_3)_2C_2H_5SiOH$ ,  $CH_3(C_2H_5)_2SiOH$ ,  $(C_2H_5)_3SiOH$  and  $C_6H_5(C_2H_5)_2SiOH$  were investigated in a range of wave lengths<sup>3</sup> of from 2 - 4 to determine the nature of molecular association of silanols and the effect of the Si-atom on the hydroxyl group. It was established, among others, that the chem. properties of silanols, particularly their amphoteric properties, are due to the strengthening of the O-H bond and strong reaction between the oxygen and hydrogen of the neighboring molecules which takes place as result of increased polarity of the O-H bond. Graphs.

Institution : Acad. of Sc., USSR, Institute of Combustible Minerals

Submitted : .....

SHOSTAKOVSKIY, M. F.

"Investigations in the Field of Alcohol Oxides. II Preparation and Properties of  $\alpha, \beta$ -Alcohol Oxides of the Aliphatic Series," Zhur. Obshch. Khim., 24, No.2, p.231, 1954

Comment B-87001, 27 Jul 55

SHOSTAKOVSKIY, M. F.

Synthesis of alkoxymethylolactams. I. Alkoxymethyl-  
denecaprolactams. M. F. Shostakovskii and F. P. Sidel-  
kovskiy. J. Gen. Chem. U.S.S.R. 24, 1633-8 (1954) (Engl. translation).—See C.A. 49, 13005b. R. M. R.

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SHOSTAKOVSKIY, M. F.

USSR/Chemistry - Vinyl compounds

Card 1/1 : Pub. 151 - 19/42

Authors : Shostakovskiy, M. F., and Sidel'kovskaya, F. P.

Title : Synthesis of alkoxyethylidene lactams. Part 1.- Alkoxyethylidene caprolactams prolactams

Periodical : Zhur. ob. khim. 24/9, 1576-1581, Sep 1954

Abstract : The products obtained from the reaction of caprolactam with alpha-chloroethylbutyl and alpha-chlorodiethyl ether are described. It was found that the addition of caprolactam to vinyl butyl ether and butanol to vinyl-caprolactam, for the purpose of synthesizing butoxyethylidene caprolactam, brings unsatisfactory results especially with regard to the yield of the product searched for. The products formed during hydrolysis of alkoxyethylidene caprolactams in the presence of sulfuric acid are listed. Seven USSR references (1946-1954).

Institution : Acad. of Sc. USSR, Institute of Org. Chem., Laboratory of Vinyl Compounds

Submitted : May 10, 1954

SHOSTAKOVSKIY, M.F.

62  
 /Oxygen-containing organosilicon compounds. III. Prepa-  
 ration of trimethyl- and triethylsilanols and their trans-  
 formations. M. F. Shostakovskii, I. A. Shchukin, D. A.  
 Kochkin, and V. I. Belyaev (N. D. Zelinskii Inst. Org.  
 Chem., Acad. Sci. U.S.S.R., Moscow). *Zhur. Obshchei*  
*Khim.* 24, 2202-8 (1964); cf. *C.A.* 49, 1641h, 7610f.  
 Into 100 g.  $\text{Me}_3\text{SiCl}$  in dry  $\text{Et}_2\text{O}$  was passed dry  $\text{NH}_3$  9  
 hrs. at  $0-7^\circ$ , the pptd.  $\text{NH}(\text{SiMe}_3)_3$  b.p.  $125-5.8^\circ$ ,  $d_4^{20}$   
 distd., yielding 64.2%.  $\text{NH}(\text{SiMe}_3)_3$  was mixed with 50 ml.  $\text{H}_2\text{O}$ ,  
 0.7764,  $n_D^{20}$  1.4090. This (70 g.) was mixed with 50 ml.  $\text{H}_2\text{O}$ ,  
 250 ml.  $\text{Et}_2\text{O}$ , and 10 drops methyl orange indicator soln.,  
 and treated with cooling to  $0-7^\circ$  with 250 ml.  $N$  HCl over  
 2.5 hrs. when the reaction was complete; distn. of the org.  
 layer gave 88.8%  $\text{Me}_3\text{SiOH}$ , b.p.  $88-8.6^\circ$ ,  $d_4^{20}$  0.8130,  $n_D^{20}$   
 1.3802. This (22.5 g.), 21 g.  $\text{EtOCH}_2\text{CH}_3$  and 0.004 g.  
 HCl were heated in sealed ampul 8 hrs. at  $65^\circ$ , yielding  
 15.3%  $\text{MeCH}(\text{OEt})\text{OSiMe}_3$ , b.p.  $38-9^\circ$ ,  $n_D^{20}$  1.3940,  $d_4^{20}$   
 0.8340, as well as 18.4 g.  $\text{O}(\text{SiMe}_3)_2$ , b.  $90-100^\circ$ , and 5.4 g.  
 $\text{MeCH}(\text{OEt})_2$ . Refluxing 151 g.  $\text{Et}_2\text{SiCl}_2$  with 102.1 g. dry  
 $\text{Ac}_2\text{O}$  8-6 hrs. with distn. of  $\text{AcCl}$ , followed by slow addn.  
 of the residue under the surface of 500 ml.  $\text{H}_2\text{O}$  and 20 ml.  
 18%  $\text{NH}_4\text{OH}$  below  $6^\circ$ , gave a top layer of  $\text{Et}_2\text{SiOH}$ , 78%,  
 b.p.  $80^\circ$ , b.m.  $153.5-4.5^\circ$ ,  $n_D^{20}$  1.4341,  $d_4^{20}$  0.8640; the same was  
 formed in 91% yield when 100 g.  $\text{Et}_2\text{SiCl}_2$  in 500 ml. dry  
 $\text{Et}_2\text{O}$  and a few drops of phenolphthalein indicator were  
 treated at  $-5$  to  $+2^\circ$  with  $N$  NaOH until a stable pink color  
 formed; distn. of the org. layer gave the final product.  
 $\text{Et}_2\text{SiOH}$  has a camphor odor, is sparingly sol. in  $\text{H}_2\text{O}$ , can be  
 stored in a well stoppered flask for long periods; on heating  
 with mineral acids it is transformed to  $\text{O}(\text{SiEt}_2)_2$ ; it does not  
 react with alkalis, but does react with Na and K on heating.  
 Heating 33 g.  $\text{Et}_2\text{SiOH}$  and 21.5 g.  $\text{PrOCH}_2\text{CH}_3$  with 0.02  
 ml. HCl in ampul 10 hrs. at  $65^\circ$  gave 67.45%  $\text{MeCH}(\text{OPr})_2$ ,  
 $\text{OSiEt}_2$ , b.p.  $80-90^\circ$ , b.m.  $204-5^\circ$ ,  $n_D^{20}$  1.4250,  $d_4^{20}$  0.8572.  
 G. M. Kosolapoff

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SHOSTAKOVSKIY, M.F.

ROZEN, B.Ya., kandidat khimicheskikh nauk (Leningrad)

Book about a famous Russian chemist ("Academician Aleksei  
Evgrafovich Favorskii. M.F.Shostakovskii. Reviewed by B.IA.Ro-  
zen). Priroda 43 no.8:122-124 Ag '54. (MLRA 7:8)  
(Favorskii, Aleksei Evgrafovich, 1860-1945) (Shosta-  
kovskii, M.F.)



SHOSTAKOVSKIY, M. F.

Chemical structure of acetals. M. F. Shostakovskii, M. I. Batuev, V. I. Belyaev, and A. D. Matveeva (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). Doklady Akad. Nauk S.S.S.R. 94, 261-4 (1954).—In view of the known reactions of acetals (elimination of phenols on heating of aromatic-aliphatic acetals, disproportionation on heating of aliphatic acetals, alcoholic reactions of aliphatic acetals) it was felt that their structures might involve tautomerism with structures like  $\text{CH}_2\text{:CHOR...HOR}$ . The following acetals were prepd. for a test of this hypothesis; the syntheses were run by the reaction of  $\text{CH}_2\text{:CHOPh}$  with  $\text{MeCOH}$  or of guaiacol with  $\text{CH}_2\text{:CHOCHMe}$  in the presence of a trace of  $\text{HCl}$ :  $\text{MeCH(OCMe}_2\text{)OPh}$ , b<sub>p</sub> 83-4°, d<sub>4</sub> 0.9593, n<sub>D</sub><sup>20</sup> 1.4836;  $\text{MeCH(OCMe}_2\text{)OC}_6\text{H}_4\text{OMe-o}$ , b<sub>p</sub> 111-12°, d<sub>4</sub> 1.0132, n<sub>D</sub><sup>20</sup> 1.4930. The intermediate  $\text{CH}_2\text{:CHOCHMe}$ , b<sub>p</sub> 75-5.2°, d<sub>4</sub> 0.7853, n<sub>D</sub><sup>20</sup> 1.3041. Raman spectra of the above acetals show many lines which exceed the sum of the lines caused by the phenol component as such and  $\text{Me}_2\text{COH}$  as such; in all instances the frequencies of these components are always present. This is believed to support the tautomerism suggested above. The double-bond line of  $\text{CH}_2\text{:CHOCHMe}$  at 1637  $\text{cm}^{-1}$  is weaker in the acetal than in the vinyl ether, as might be expected from the concept of tautomerism.

G. M. Kosolapoff

SHOSTAKOVSKIY, M. F.

USSR.

✓ Chemical and physical properties of the hydroxyl group in trimethylsilanol. M. I. Batuev, M. F. Shostakovskii, V. I. Belyayev, A. D. Matveeva, and E. V. Dubrova (N.D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 95, 531-4 (1954).  $\text{Me}_3\text{SiOH}$ , m.  $-4.5^\circ$ , bp  $98-8.2^\circ$ ,  $n_D^{20}$  1.3892,  $n_D^{25}$  1.3871,  $d_4^{25}$  0.8146,  $d_4^{20}$  0.8085, maintains its H-bond formation ability in soln., as shown by cryoscopic detns.; in CCl<sub>4</sub>, it forms assoc. complexes with a rapid rise of apparent mol. wt. with the concn. (shown graphically) to over that of a dimeric structure. Hence in the pure liquid more complex structures can be postulated. In the liquid state the Raman spectrum is

given.  $\text{Me}_3\text{COH}$  also shows a wide HO band caused by H bonding. However, the fine structure in the Si deriv. indicates a greater acidic nature of the HO in the Si deriv. than in the C analog.  $\text{Me}_3\text{SiOH}$  reacts more vigorously with Na and K at  $0-3^\circ$  than does the carbinol.  $\text{Me}_3\text{SiOH}$  also forms a ppt. of  $\text{Me}_3\text{SiONa}$  with concd. NaOH. With traces of acid catalyst  $\text{Me}_3\text{SiOH}$  adds to vinyl ethers, forming acetals (cf. Shostakovskii, *et al.*, *C.A.* 49, 1542a). However,  $\text{Me}_3\text{SiOH}$  also displays basic properties of the HO group, particularly shown by the Raman lines 3632 and 3702  $\text{cm}^{-1}$ ; in CCl<sub>4</sub> the characteristic HO band vanishes and only the 3702 line remains; this must be due to the vibration of the unassoc. HO group. It is shifted in respect to that of C analog because of the electronegativity difference of Si.

G. M. K.

SHOSTAKOVSKIY, M. F.

# U S S R .

✓ Oxygen-containing organosilicon compounds. Preparation of diethylphenylchlorosilane, diethylphenylsilanol, tetraethyldiphenyldisiloxane, and some of their transformations. M. F. Shostakovskii and D. A. Kochkin (N. D. Zelinskii Inst. Org. Chem., Acad. Sci., U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 95, 821-4 (1954).  $\text{Et}_2\text{SiCl}_2$  (157 g.) with either  $\text{PhMgBr}$  or  $\text{PhLi}$  (from 157 g.  $\text{PhBr}$ ) in  $\text{Et}_2\text{O}$  gave 80%  $\text{Et}_2\text{PhSiCl}$ ,  $b_p$  228°,  $n_D^{20}$  1.5130,  $d_4^{20}$  1.0252. When this (100 g.) in 500 ml.  $\text{Et}_2\text{O}$  with a little phenolphthalein was treated with  $\text{N NaOH}$  until the pink color persisted, the org. layer and  $\text{Et}_2\text{O}$  ext. of the aq. layer gave 91%  $\text{Et}_2\text{PhSiOH}$ ,  $b_p$  107.5-10°,  $n_D^{20}$  1.5170,  $d_4^{20}$  0.9905. Refluxed 2-3 hrs. with a few drops concd.  $\text{HCl}$ , this gave  $(\text{Et}_2\text{PhSi})_2\text{O}$ ,  $b_p$  210-18°,  $n_D^{20}$  1.5214,  $d_4^{20}$  0.9323. Heating 11 g.  $\text{BuOCH}_2\text{CH}_3$  and 9 g.  $\text{Et}_2\text{PhSiOH}$  with 0.02 ml.  $\text{H}_2\text{SO}_4$  1-1.5 hrs. on a steam bath gave after neutralization with  $\text{K}_2\text{CO}_3$  a no. of fractions which yielded 54.5%  $\text{Et}_2\text{PhSiOCHMeOBu}$ ,  $b_p$  120-3°,  $n_D^{20}$  1.4776,  $d_4^{20}$  0.9377. G. M. Kosolapoff.

SHOSTAKOVSKIY, M. F.

USSR.

Synthesis and transformations of vinyl ethers of higher polyatomic alcohols and cellulose. Tetravinyl ether of Me  $\alpha$ -glucoside. M. F. Shostakovskii, E. N. Pilezhnera, and L. V. Tsymbal (N.D. Zeldinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 96, 99-102 (1954).—Almost no vinylation of Me  $\alpha$ -glucoside takes place in the reaction with  $C_2H_4$  below 125°; above 150° colored products form; from several such runs there was obtained a small amount of a blue substance, b, 133-5°,  $n_D^{20}$  1.4920,  $d_4^{20}$  1.1937, which appeared to be  $C_{12}H_{20}O_6 \cdot CrH_2$ . Probably the best vinylation technique was as follows: 60 g. Me  $\alpha$ -glucoside, 12 g. KOH and 350 ml. dioxane was satd. with  $C_2H_4$  in an autoclave at room temp. then heated 11 hrs. to 125-45° with 133 g.  $C_2H_4$  being added to the app. Distn. of the product gave 84.8% tetravinyl ether of methyl glucoside, b, 138-40°; after redistn. from Na the product b, 138-8.5°, m. 43-6°,  $[\alpha]_D^{25}$  140.3° ( $CCl_4$ ),  $n_D^{20}$  1.4820,  $d_4^{20}$  1.1029, it supercools easily. Shaking the product with 3.5% HCl gave AcH and methyl glucoside in 24 hrs. at room temp.

G. M. Kosolapoff

SHOSTAKOVSKIY, M. F.

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Polymerization of vinyl compounds. I. Stepwise synthesis of polyvinyl butyl ether. M. F. Shostakovskiy and V. A. Gladyshevskaya (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1955, 140-5; *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1955, 121-5; cf. 49, 4508a. A synthesis of products of progressively higher complexity and chain length in the formation of polymer of BuOCH=CH<sub>2</sub> was achieved. To 174 g. MeCH(OBu)<sub>2</sub> was added 4 g. 5% FeCl<sub>3</sub> in BuOH and the mixt., at 48-50°, was treated with 50 g. BuOCH=CH<sub>2</sub> dropwise while maintaining a temp. of 50°; after 1 hr. at 50° the catalyst was pptd. with powd. Na<sub>2</sub>CO<sub>3</sub>, the mixt. stirred 3 hrs., filtered and distd. yielding 62.3 g. MeCH(OBu)CH<sub>2</sub>CH(OBu)<sub>2</sub> (I), b<sub>p</sub> 131-5°, d<sub>4</sub> 0.8855, n<sub>D</sub><sup>20</sup> 1.4255 (viscosity 3.573 centipoises at 20°), and some 0.6 g. MeCH(OBu)CH<sub>2</sub>CH(OBu)CH<sub>2</sub>CH(OBu)<sub>2</sub> (II), b<sub>p</sub> 175-7°, d<sub>4</sub> 0.8886, n<sub>D</sub><sup>20</sup> 1.4346. I and BuOCH=CH<sub>2</sub> treated similarly gave II and some MeCH(OBu)CH<sub>2</sub>CH(OBu)CH<sub>2</sub>CH(OBu)CH<sub>2</sub>CH(OBu)<sub>2</sub> (III), b<sub>p</sub> 95-7°, d<sub>4</sub> 0.9033, n<sub>D</sub><sup>20</sup> 1.4435. II and BuOCH=CH<sub>2</sub> gave III and a residue of higher undistillable products. I, II and III are readily hydrolyzed in aq. medium in the presence of NaHSO<sub>4</sub>.

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G. M. Kosolapov

SHOSTAKOVSKIY, M.F.

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✓ Synthesis of sulfur compounds based on vinyl ethers and acetylene. XI. Ionic transformations of vinyl ethyl sulfide. M. F. Shostakovskiy, E. N. Prilezhnaya, and N. I. Uvarova (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1955, 184-82; *Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci.* 1955, 135-41; cf. C.A. 49, 9483a. Heating  $\text{EtSCH:CH}_2$  with 0.5N  $\text{NH}_4\text{OH}\cdot\text{HCl}$  2 hrs. at  $30^\circ$  gave but 3.9-4.1% hydrolysis (estd. by titration of liberated  $\text{HCl}$ ); in 24 hrs. at  $20-30^\circ$  this reached 57-67%, while 0.5 hr. at  $100^\circ$  gave 71.4-72.6% hydrolysis. Hydrolysis with 5%  $\text{HCl}$  in aq. dioxane 6 hrs. at  $100^\circ$  gave 76%  $\text{MeCH}(\text{SEt})_2$ ,  $b_p$   $65-6^\circ$ ,  $n_D^{20}$  1.5023. After 1 hr. of acid-catalyzed hydrolysis the results approx. a reaction:  $2 \text{EtSCH:CH}_2 + \text{H}_2\text{O} \rightarrow \text{MeCHO} + \text{MeCH}(\text{SEt})_2$ , although the latter is also hydrolyzed further to  $\text{EtSH}$  and  $\text{AcH}$  in an apparently reversible reaction, some 34-5% hydrolysis occurring in 11 hrs. at  $100^\circ$ .  $\text{EtSCH:CH}_2$  (6 g.) and 4.8 g.  $\text{EtOH}$  treated with  $\text{SO}_2$  for 5 min. at  $-10^\circ$  then kept 2.5 hrs. at  $24^\circ$  and left overnight, then heated 5 hrs. at  $60^\circ$ , gave 50%  $\text{MeCH}(\text{SEt})_2$ ,  $\text{MeCH}(\text{OEt})_2$ , and  $\text{EtOH}$ . In a similar reaction in which a small amt. of  $\text{HCl}$  in dioxane was added to the reac-

tion mixt. and the latter heated 1.5 hrs. at  $55-60^\circ$ , gave  $\text{EtOH}$ ,  $\text{MeCH}(\text{OEt})_2$ ,  $\text{EtSH}$  and a small amt. of  $\text{MeCH}(\text{SEt})_2$ ,  $b_p$   $66.5-7^\circ$ ,  $n_D^{20}$  1.4451,  $d_4^{20}$  0.9038. The yield of the latter declines to 10-11% if the catalyst is aq. 30%  $\text{HCl}$  in the presence of dioxane, while the use of  $\text{MeCHBr}\cdot\text{SEt}$  as the catalyst gave also a 10% yield of the mixed acetal.  $\text{MeCH}(\text{SEt})_2\text{OEt}$  (0.5 g.) and 4.8 g.  $\text{EtOH}$  treated 5 min. with  $\text{SO}_2$  at  $0^\circ$  then heated 1.5 hrs. at  $60-6^\circ$  and kept 2 days, gave  $\text{EtSH}$  and some  $\text{MeCH}(\text{OEt})_2$ , along with unidentified products. Passage of dry  $\text{HCl}$  into  $\text{EtSCH:CH}_2$  at  $-10^\circ$  gave 80.9%  $\text{EtSCH:CH}_2$ ,  $b_p$   $46-7^\circ$ ,  $n_D^{20}$  1.4705,  $d_4^{20}$  1.012, which treated with  $\text{H}_2\text{O}$  hydrolyzed nearly completely in 15 min. to  $\text{AcH}$  and  $\text{HCl}$  and  $\text{MeCH}(\text{SEt})_2$ . Dry  $\text{HBr}$  and  $\text{EtSCH:CH}_2$  gave 77.1%  $\text{EtSCHBrMe}$ ,  $b_p$   $39-41.5^\circ$ ,  $n_D^{20}$  1.5130,  $d_4^{20}$  1.3677, which fumes in air and can be stored only in abs.  $\text{Et}_2\text{O}$ . If the addn. of  $\text{HBr}$  is made in pentane in the presence of a little  $(\text{NCMe}_2\text{CN})_2$  under  $\text{N}_2$ , the reaction being completed by 2 hrs. at  $60-70^\circ$ , the same product forms in 79.6% yield.  $\text{EtSCHBrMe}$  reacts rapidly with  $\text{H}_2\text{O}$  and in 15 min. yields nearly 100%  $\text{HBr}$ ,  $\text{AcH}$  and  $\text{MeCH}(\text{SEt})_2$ . G. M. Kosolapoff

SHOSTAKOVSKIY, M.F.

V Optical study of some vinyl ethers of ethanolamines. M. F. Shostakovskiy, M. I. Batuev, I. A. Chekulacva, and A. D. Matveeva (N. D. Zelinskii Inst., Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvst. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci.* 1955, 481-6 (Engl. translation), 644-50; cf. C.A. 49, 7388b. —The previously reported vinyl ethers of ethanolamine and its analogs display the Raman characteristics of intramol. H bonds; the chem. inertness of some compds. in this group is ascribed to H bonding. The region of diffuse Raman lines at 3150-3400 cm.<sup>-1</sup> includes the O—H—O, as well as N—H—O bonds. The following Raman spectra are reported: CH<sub>2</sub>:CHOCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, 169(2), 248(4b), 285(0), 324(2), 352(2), 404(1), 435(1), 498(4), 603(3), 644(0), 710(2), 831(5b), 904(4), 960(4), 996(4), 1084(2), 1099(3), 1113(3), 1157(1), 1179(2), 1209(2), 1321(10), 1354(2), 1407(2), 1481(5), 1617(8), 1637(7), 2871(7), 2932(8b), 3018(3), 3217(0), 3263(1), 3293(1), 3324(8b), 3385(3b); (CH<sub>2</sub>:CHOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NH, 171(2), 241(4b), 503(3), 609(3), 660(0), 745(0), 778(0), 828(5b), 893(3), 935(0), 972(3), 1001(2), 1032(3), 1067(2), 1102(2), 1149(3), 1203(3), 1263(3), 1322(10), 1364(0), 1389(1), 1413(2), 1463(3), 1617(8), 1642(7), 2842(2), 2876(7), 2938(8b), 3022(4).

3225(0), 3271(1), 3338(4b); CH<sub>2</sub>:CHOCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CHMeCO<sub>2</sub>Me, 163(1), 188(1), 236(8b), 324(1), 366(1), 431(0), 468(0), 505(1b), 611(0b), 668(0b), 708(1), 768(1), 813(1), 838(0b), 903(2b), 935(0), 973(3), 991(3), 1029(0), 1058(0), 1104(1), 1152(1b), 1208(1b), 1321(10), 1354(1), 1419(1), 1463(8), 1616(8), 1637(5), 1660(2), 1688(1), 1737(4), 2880(0), 2943(10b), 2972(3), 3020(2), 3032(0), 3179(1), 3224(1), 3274(1), 3343(4b); PhNHCH<sub>2</sub>CH<sub>2</sub>OCH:CH<sub>2</sub>, 125(3), 178(1), 214(2), 233(2), 248(2), 414(4b), 490(1), 510(1), 531(1), 578(0), 598(1), 619(4), 648(0), 663(0), 752(4), 782(4), 815(5), 832(0), 852(5), 871(0), 916(1), 953(10), 1029(5), 1073(0), 1155(4), 1182(3), 1199(0), 1287(1), 1320(5), 1356(0), 1380(0), 1408(0), 1434(0), 1455(1), 1493(1), 1603(10), 1616(1), 1639(1), 2850(0), 2876(4), 2933(4), 2984(0), 3024(1), 3351(1), 3351(1), 3406(4b); HOCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, 171(1), 482(4), 523(3), 838(4), 874(5), 1034(3), 1065(4), 1083(5), 1108(4), 1173(2b), 1248(3b), 1298(5), 1313(5), 1358(4b), 1400(10), 1593(1b), 2707(3b), 2862(10), 2914(9), 2942(9), 3145(1), 3187(3), 3239(2), 3300(8b), 3364(3b), 3150-3400 (HO band).

G. M. Kosolapov

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SHOSTAKOVSKIY, M.F.

✓ Reactions of vinyl and polyfunctional compounds. VI.  
Reaction of vinyl ethers with pentaerythritol. M. F.  
Shostakovskii, A. S. Atavin, and V. V. Zhebrovskii (N. D.  
Zelinskii Inst. Org. Chem. Acad. Sci. U.S.S.R., Moscow).  
Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1955,  
539-43; Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. 1955,  
477-80 (Engl. translation); cf. C.A. 50, 4768b. — Mixing  
20 g.  $C(CH_2OH)_4$  (I), 75.3 g.  $EtOCH_2CH_3$ , and 6 drops HCl  
gave an exothermic reaction which yielded  $EtOH$ ,  $MeCH$ -  
 $(OEt)_2$ , much resin, and 13 g.  $MeCH(OCH_2)_2C(CH_2O)_2$ -  
 $CHMe$  (II), m.  $40^\circ$  (from  $EtOH$ ), b.  $100-10^\circ$ . I with  $BuO$ -  
 $CH_2CH_3$  gave similarly  $BuOH$ ,  $MeCH(OBu)_2$ , and II.  
I (20 g.) and 70.4 ml.  $BuOCH_2CH_3$  with 15 drops HCl  
gave  $BuOH$ ,  $MeCH(OBu)_2$ , and 21 g. II. G. M. K.

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SHOSTAKOVSKIY, M. F.

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1/Reactivity of vinyl compounds and its manifestation in mechanisms of polymerization reactions. M. F. Shostakovskii. Vopr. Khim. Kinetiki, Kataliza i Reaktivnosti, Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 1953, 793-809; cf. C.A. 48, 12455f. --Review of ionic and radical addns. of vinyl compds. 20 references. G. M. Kosolapoff

SHOSTAKOVSKIY, M.F.

Synthesis of sulfur compounds based on vinyl ethers and  
acetone. XIII. General method of synthesis of thio-  
vinyl ethers. M. F. Shostakovskii, E. N. Prilezhayeva, and  
N. I. Uvarova. Bull. Acad. Sci. U.S.S.R. Div. Chem.  
Sci. 1955, 821-7 (Engl. translation).—See C.A. 50, 9278c.  
B. M. R.

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SHOSTAKOVSKIY, M. F.

3

✓ Synthesis and transformations of vinyl ethers of ethanol-  
amines. VII. The vinyl ether of 2-(diphenylamino)ethanol.  
M. F. Shostakovskii and I. A. Cherkutskaya. *Bull. Acad.  
Sci. U.S.S.R., Div. Chem. Sci.* 1955, 829-33 (Engl. transla-  
tion).—See *C.A.* 50, 9325c. B. M. R.

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SHOSTAKOVSKIY, M.F.

✓ Chemical transformations on unsaturated and high-molecular weight compounds. VI. Copolymerization of vinylcaprolactam and methyl methacrylate in the presence of benzoyl peroxide and the dinitrile of 2,2'-azodisobutyric acid. M. F. Shostakovskii, P. P. Shchel'kovskaya, and A. M. Khomutov, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1955, 836-40 (Engl. translation).—See C.A. 50, 6292a. B. M. R.

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SHOSTAKOVSKIY, M. F.

*Chem* ✓ Synthesis and transformations of ~~oxygen-containing~~  
organosilicon compounds. II. Reaction of diethyl- and  
diphenylsilanediols with vinyl ethers. M. F. Shosta-  
kovskii, D. A. Kochkin, and V. M. Rog. *Bull. Acad. Sci.*  
U.S.S.R., Div. Chem. Sci. 1955, 871-3 (Engl. translation).  
See C.A. 50, 9320d. B. M. R.

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M. A. YOUT 2  
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*Chem*  
 ✓ Synthesis of sulfur compounds based on vinyl ethers and  
 acetylene. XIII. A general method of synthesis of thio  
 vinyl ethers. M. F. Shostakovskiy, E. N. Prilezhneva, and  
 N. I. Uvarova (N. D. Zelinski Inst. Org. Chem., Moscow).  
 Izvest. Akad. Nauk S.S.S.R., *Oldel. Khim. Nauk* 1955, 906-  
 12; cf. C.A. 50, 7080f. — BuSH (106.5 g.), 180 g. dioxane,  
 and 13.2 g. KOH (20 mole-%) satd. with  $C_2H_2$  in an auto-  
 clave in the cold, an  $C_2H_2$  pressure of about 30 atm. then  
 maintained 1 hr. at 70-90°, the mixt. dild. with  $Et_2O$ ,  
 washed with  $H_2O$ , and the org. layer distd. gave a series of  
 fractions from which were isolated 96 g.  $BuSCH:CH_3$ , b.p.  
 47.5-48.5°,  $n_D^{20}$  1.4722,  $d_4^{20}$  0.8693, and 7.5% ( $CH_3SBu$ ).  
 The use of an aq. soln. in the reaction gave but 30% of the  
 sulfide, while  $BtOH$ ,  $MePh$ , or  $C_6H_6$  gave zero yields.  
 Similarly were obtained the following  $RSCH:CH_3$  (R, %  
 yield, b.p./mm.,  $d_4^{20}$ , and  $n_D^{20}$  given): Pr, 60, 43.6°/50,  
 0.8723, 1.4734; Et, 61, 91.9-2.2°/780, 0.8767, 1.4759;

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# SYNTHESIS OF SULFUR

iso-Am, 65, 53.5-4.5°/17, 0.8615, 1.4704;  $PhCH_2$ , 76.2, 90-90.5°/7, 1.0347, 1.5794;  $Ph$ , 71.6, 76.5°/4, 1.0417, 1.5838 (this is best run in BuOH 3 hrs. at 145-60°). The disulfides are best obtained by mixing the corresponding mercaptans and thio vinyl ethers in contact with air; the reaction, which commences in a few min., is exothermic and cooling to 20-5° is advised, after which the mixt. is kept overnight and is distd. Thus were obtained (% yield, b.p./mm.,  $n_D^{20}$ , and  $d_4^{20}$  given):  $EtOCH_2CH_2SPh$ , 100, 98.5°/3.5, 1.5013, 0.9539;  $(CH_3SPH)_2$ , 100, 67.5°, —, —;  $BuSCH_2CH_2SCH_2CH_2OBu$ , 90, 155°/4, 1.4900, 0.9600;  $(CH_3SPH)_2$ , —, 91-2.5°/3, 1.5046, 0.9565;  $(CH_3SPh)_2$ , —, 131-2°/6, 1.4967, 0.9355. The vinyl thio ethers are quantitatively cleaved by  $HgCl_2$  in EtOH so that this reaction may be used for analytical titration of such compds., yielding  $RSHgCl$ ,  $HCl$ , and  $MeCH(OEt)_2$ . G. M. Kosolapoff

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SHOSTAKOVSKIY, M. F.

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 ✓ Synthesis and transformations of vinyl ethers of ethanol-  
 amines. VII. The vinyl ether of 2,2-diphenylamino)-  
 ethanol. M. F. Shostakovskii and I. A. Cherkulaeva (N. D.  
 Zelinskii Inst. Org. Chem., Moscow). *Izvest. Akad.  
 Nauk S.S.S.R., Otdel. Khim. Nauk* 1955, 913-18; cf. *C.A.*  
 49, 15489i; 50, 1822f. Heating  $\text{Ph}_2\text{NCH}_2\text{CH}_2\text{OH}$  with ethylene oxide  
 in an autoclave to 220-40° gave 60-5%  $\text{Ph}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$   
 (I), b<sub>p</sub> 183-0°, d<sub>4</sub> 1.121, n<sub>D</sub><sup>20</sup> 1.6210. This (73 g.), 8 g.  
 IR, salt, 200 ml.  $\text{C}_6\text{H}_6$ , and 14-16 atm.  $\text{C}_6\text{H}_6$  gave, after 3 hrs.  
 at 180°, 74.5%  $\text{Ph}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$ : CH<sub>3</sub>, b<sub>p</sub> 163-0°, n<sub>D</sub><sup>20</sup>  
 1.5980, d<sub>4</sub> 1.0696. In dioxane soln. the yield reaches 81.5%;  
 the use of KOH catalyst gave 62-66.5% yields in  $\text{C}_6\text{H}_6$ .  
 The ether hydrolyzes with 2%  $\text{H}_2\text{SO}_4$  at 95° to  $\text{AcH}$  and I.  
 Hydrogenation of I over Raney Ni gave  $\text{Ph}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$ .  
 b<sub>p</sub> 158-9°, n<sub>D</sub><sup>20</sup> 1.5920, d<sub>4</sub> 1.0800.  $\text{Ph}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$   
 (3.7 g.) and 7.2 g. I treated with 1 drop concd.  $\text{HCl}$ , and  
 kept 4 hrs. after the exothermic reaction yielded 62.5%  
 $\text{MeCH}(\text{OCH}_2\text{CH}_2\text{NPh}_2)_2$  (II), b<sub>p</sub> 282-4°, n<sub>D</sub><sup>20</sup> 1.6185, d<sub>4</sub>  
 1.1175. Similarly the vinyl ether with BuOH gave  $\text{MeCH}(\text{OCH}_2\text{CH}_2\text{NPh}_2)_2$   
 (OBu)<sub>2</sub> and II, as well as a wide fraction of materials which  
 decompd. during distn., yielding  $\text{BuOCH}_2\text{CH}_2$  and I. A  
 similar reaction with MeOH gave II and  $\text{MeCH}(\text{OMe})_2$ , as  
 well as decompn. products, including I.  $\text{FeCl}_3$  (5% in Bu-  
 OH) polymerizes  $\text{Ph}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$  to 29% of a  
 viscous dark liquid, mol. wt. about 600; concd.  $\text{HCl}$  gives  
 about 31% polymer, mol. wt. 420-60;  $(\text{:NCMeCN})_2$   
 polymerizes the vinyl ether to a yellow oil, mol. wt. 475, in:  
 a very low yield after 100 hrs. at 60°. G. M. K.

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SHOSTAKOVSKIY, M F.

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Chemical transformations on unsaturated and high-molecular weight compounds. VI. Copolymerization of vinylcaprolactam and methyl methacrylate in the presence of benzoyl peroxide and the dinitrile of 2,2'-azodiisobutyric acid. M. F. Shostakovskii, F. P. Sidel'kovskaya, and A. M. Khomutov (N. D. Zelinskii Inst. Org. Chem., Moscow). *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1955, 919-21; cf. *C.A.* 47, 9917g; 48, 6159c; 50, 1074h. Vinylcaprolactam and  $\text{MeO}_2\text{CCMe:CH}_2$  were copolymerized in the presence of either  $\text{Bz}_2\text{O}_2$  or  $(:\text{NCMe:CN})_2$  in various proportions of the monomers. The content of methacrylate links in the copolymers ranged from 85.7 to 27.6 mole-%. The products were sol. in  $\text{Me}_2\text{CO}$ ,  $\text{C}_6\text{H}_6$ , and  $\text{EtOH}$  but insol. in  $\text{Et}_2\text{O}$ ; those with high content of methacrylates were insol. in  $\text{H}_2\text{O}$ . The polymerizations were run at  $60^\circ$  for 48-72 hrs. with 0.2% initiator. The copolymers appeared to be inhomogeneous in their behavior with solvents, but no polymers of the initial monomers alone were found.

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G. M. Kosolapoff

SHOSTAKOVSKIY, M. F.

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 ✓ Synthesis and transformations of oxygen-containing organosilicon compounds. II. Reaction of diethyl- and diphenylsilanediols with vinyl ethers. M. F. Shostakovskii, D. A. Kochkin, and V. M. Roz (N. D. Zelinskii Inst. Org. Chem., Moscow). *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1953, 953-5; cf. *C.A.* 50, 5550d.  $\text{Et}_2\text{Si}(\text{OH})_2$  (12 g.) and 50 g.  $\text{BuOCH}=\text{CH}_2$  treated with 1 drop concd.  $\text{HCl}$  and heated 1.5-2 hrs. at  $60^\circ$  yielded 37%  $\text{Et}_2\text{Si}(\text{OCHMeOBu})_2$ , b<sub>p</sub> 127-9°,  $n_D^{20}$  1.4370,  $d_4^{20}$  0.9010, and a residue of polysiloxanes. The product treated with 5%  $\text{H}_2\text{SO}_4$  3-4 hrs. at  $100^\circ$  gave 95-98%  $\text{AcH}$ . Similar reaction of  $\text{Ph}_2\text{Si}(\text{OH})_2$  with  $\text{BuOCH}=\text{CH}_2$  gave  $\text{MeCH}(\text{C}_4\text{H}_9)$  and a high-boiling material from which it was impossible to isolate the expected silanoacetal  $\text{Ph}_2\text{Si}(\text{OCHMeOBu})_2$  owing to its thermal instability. Hydrolysis with dil. acid readily gave 82-83%  $\text{AcH}$ .  
 G. M. Kosolapoff

Chem  
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*Shostakovskiy, M. F.*

USSR/Chemistry - Conversions

Card 1/1 Pub. 40 - 16/27

Authors : Shostakovskiy, M. F., and Khomutov, A. M.

Title : Study of chem. conversions of unsaturated and high-molecular compounds.  
Part 4. Copolymerization of certain vinyl compounds with monovinyl ether  
of ethylene glycol

Periodical : Izv. AN SSSR. Otd. khim. nauk 1, 126-132, Jan-Feb 1955

Abstract : The characteristics of copolymerization reactions of monovinyl ether of ethylene glycol with methacrylic acid, its methyl ether and styrene are explained. The synthesis of copolymers of methacrylic acid and its methyl ether with monovinyl ether of ethylene glycol is described. The effect of a monovinyl ether increase in the reaction medium on the yield of copolymers is discussed. It is shown that styrene monovinyl ether of ethylene glycol so not form copolymers in the presence of benzoyl peroxide. Nine Russian and USSR references (1869-1954). Tables.

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Inst. of Org. Chem.

Submitted : September 25, 1953

*Shostakovskiy, M. F.*

USSR/Chemistry - Conversions

Card 1/2

Pub. 40 - 17/27

Authors : Shostakovskiy, M. F., and Khomutov, A. M.

Title : ~~Vinyl ethers~~ Chemical conversions of unsaturated and high-molecular compounds. Part 5.  
Copolymerization of methyl ether of acrylic acid and vinyl ethers

Periodical : Izv. AN SSSR. Otd. khim. nauk 1, 133-139, Jan-Feb 1955

Abstract : The conditions favorable for the copolymerization of methyl ether of acrylic acid (methyl acrylate) with vinyl ethyl, vinyl-n-butyl and vinyl phenyl ethers are described. It is shown that the composition of the copolymers depends largely upon the vinyl ether and methyl acrylate concentrations in the reaction mixture.

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Inst. of Org. Chem.

Submitted : December 23, 1953

Card 2/2      Pub. 40 - 17/27

Periodical :    Izv. AN SSSR. Otd. khim. nauk 1, 133-139, Jan-Feb 1955

Abstract :      Methyl acrylate and vinyl ether copolymers were found to possess  
a greater number of vinyl ether rings in their composition than the  
copolymers formed by methyl metacrylate and vinyl ethers. Nine  
references: 8 Russian and USSR and 1 USA (1869-1954). Tables

*Shostakovskiy, M. F.*

USSR/Chemistry - Polymerization

Card 1/2      Pub. 40 - 18/27

Authors :      Shostakovskiy, M. F., and Gladyshevskaya, V. A.

Title :      Polymerization of vinyl compounds. Part 1. Multistage synthesis of poly-vinylbutyl ether.

Periodical :      Izv. AN SSSR. Otd. khim. nauk 1, 140-145, Jan-Feb 1955

Abstract :      Experimental data are presented regarding the multistage synthesis of individual products of various complexity and closely related to polyvinylbutyl ether. The distinguishable characteristics of chain free-radical and ion reactions, resulting in the formation of only high molecular compounds regardless of reaction time, are analyzed.

Institution :      Acad. of Sc., USSR, The N. D. Zelinskiy Inst. of Org. Chem.

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Periodical :    Izv. AN SSSR. Otd. khim. nauk 1, 140-145, Jan-Feb 1955

Abstract :      It is pointed out that free-radical chain polymerization occurs as  
result of opening the double bonds and consequent addition of molecules.  
The mechanism of ion-chain polymerization of vinyl compounds is explained.  
Some products obtained from multistage synthesis are described. Ten  
references: 1 USA and 9 USSR (1935-1954). Table



*Shostakovskiy, M. F.*

USSR/ Chemistry - Synthesis and conversion

Card 1/2      Pub. 40 - 19/27

Authors : Shostakovskiy, M. F., and Chekulayeva, I. A.

Title : Synthesis and conversions of vinyl ethers of ethanolamines. Part 6.  
Vinyl ether of beta-(phenylamino)ethanol

Periodical : Izv. AN SSSR. khim. nauk 1, 146-153, Jan-Feb 1955

Abstract : A study of chemical conversions of vinyl ether of beta-(phenylamino) ethanol showed that the compound investigated experiences a series of conversions when subjected to the effect of concentrated hydrochloric acid resulting in the formation of 2-methyl-3-phenylloxolidine, beta-(phenylamino)ethanol and a  $C_{12}H_{15}ON$  compound.

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Inst. of Organ. Chem.

Submitted : December 23, 1953

Card 2/2      Pub. 40 - 19/27

Periodical :    Izv. AN SSSR. Otd. khim. nauk 1, 146-153, Jan-Feb 1955

Abstract :     The results obtained from the vinylation of beta-(phenylamino)ethanol showed that this compound easily converts into cyclic acetal. Sixteen references: 12 USSR, 2 German and 2 USA (1901-1954). Tables

*Shostakovskiy, M. F.*

USSR/ Chemistry - Synthesis and conversion

Card 1/2      Pub. 40 - 20/27

Authors      :    Shostakovskiy, M. F.; Prilezhayeva, Ye. N.; and Uvarova, N. I.

Title        :    ~~Synthesis of sulfuric substances~~  
Synthesis of sulfurous substances on the vinyl ether and acetylene basis.  
Part 11. Ion conversions of vinylethyl sulfide

Periodical   :    Izv. AN SSSR. Otd. khim. nauk 1, 154-162, Jan-Feb 1955

Abstract     :    It is shown experimentally that ion reactions of vinylethyl sulfide with water, alcohol and halogen hydracid have a certain inherent specificity but by their general nature are closely analogous to vinyl allyl ethers. The conditions most favorable for the hydrolysis of vinylethyl sulfide were established, together with the conditions leading to the addition of

Institution :    Acad. of Sc., USSR, The M. D. Zelinskiy Inst. of Org. Chem.

Submitted   :    November 14, 1953

Card 2/2 Pub. 40 - 20/27

Periodical : Izv. AN SSSR. Otd. khim. nauk 1, 154-162, Jan-Feb 1955

Abstract : the alcohol to the vinylethyl sulfide and the formation of monothioacetal. The conditions most suitable for the hydrohalogenation of vinylethyl sulfide are described. Thirteen references: 8 USSR, 2 USA, 2 German and 1 Dutch (1889-1954). Tables